

APPENDIX B. INITIAL PROCEDURE FOR IR METHOD  
AND ARCO RESULTS



September 7, 1990

## Standard Test Method for the Determination of the Aromatic Content of Diesel Fuels by Infrared Spectroscopy

### 1. Scope.

1.1 This test method provides for the determination of the total vol% of aromatic compounds in motor diesel fuels by infrared spectroscopy (IR) or Fourier-Transform Infrared Spectroscopy (FTIR). The range of concentration determined is from 3 to 60 volume percent.

1.2 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

### 2. Referenced Documents.

#### 2.1 ASTM Standards

D 1319 Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

E 168-67 Standard Recommended Practices for General Techniques of Infrared Quantitative Analysis

### 3. Summary of Test Method.

3.1 A small amount of fuel is introduced into a transmission cell of known path length, or placed on a horizontal attenuated total reflectance (ATR) sampler, and an infrared spectrum obtained using either infrared or FTIR, to include the area from 1700 to 1400 wavenumbers. The area between 1650 and 1555 is integrated, and the area related to the aromatics content of the diesel fuel.

#### 4. Significance and Use.

4.1 The aromatic hydrocarbon content of middle distillate fuels (diesel, jet, heating oil) is a significant factor in their combustion properties.

4.2 Appropriate analytical methods are required in order to conform to new governmental regulations limiting aromatic content of motor diesel fuels. Both regulatory bodies and producers of diesel fuels will require similar methods for use in process and quality control.

4.3 This test method is applicable to materials in the boiling range of motor diesel fuels and to dark colored materials.

4.4 Results obtained by this test method are statistically more precise than those obtained from Test Method D 1319-84, and require much shorter analysis times.

#### 5. Apparatus.

5.1 FTIR, capable of producing a computer file ready for further analysis, and capable of integrating area between two baseline points.

#### 6. Reagents and Materials.

6.1 Mineral Oil - A paraffinic reagent or medical grade oil.

6.2 Isooctane, hexane, or heptane - Reagent grade

6.3 Toluene - Reagent grade

#### 7. Preparation of Apparatus.

7.1 Clean the ATR cell or transmission cell between samples with isooctane, heptane, or hexane until no oily residue from previous samples remains. If necessary, use another solvent such as toluene to insure cleanliness of the cell. Use only soft tissue to blot and gently wipe fluids from ATR crystal, if using that method.

7.2 Use manufacturer instructions regarding calibration and maintenance of instrument.

8. Procedure A, using horizontal ATR sampler.

8.1 Run a background on the infrared instrument with no sample in place, and with the cell scrupulously clean. Store background for reference use in sample spectra.

8.2 Obtain a spectrum of mineral oil over the range 1700 to 1400 and measure the area of the aromatic band at 1650 to 1555 wavenumbers, relative to the background. Set up the procedure to make the baseline effectively zero at 1650 and 1555 wavenumbers, either by setting the baseline to zero at those points, or by drawing a point to point baseline across the points and integrating the net area over the region. Do the same for the area between 1650 and 1625 to account for the olefin region of the band. Record both these areas for each sample.

8.3 Clean the ATR cell carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove sample film completely. Take fresh background immediately before running fuel samples. Run as for mineral oil above. Repeat for each sample to be run.

9. Procedure B, using transmission cell.

9.1 Obtain a background with no sample holder in the sample chamber. New backgrounds should be acquired regularly, every hour of sample running.

9.2 Obtain a spectrum of mineral oil over the range 1700 to 1400, and measure the area of the aromatic band at 1650 to 1555 wavenumbers, relative to the background. Set up the procedure to make the baseline effectively zero at 1650 and 1555 wavenumbers, either by setting the baseline to zero at those points, or by drawing a point to point baseline across the points and integrating the net area over the region. Do the same for the area between 1650 and 1625 to account for the olefin region of the band. Record both these areas for each sample.

9.3 Clean cell completely and carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove sample film completely. Obtain a spectrum of the fuel sample relative to the background. Continue the operation for the samples to be analyzed, cleaning the cell well between samples and obtaining frequent fresh backgrounds in case of staining or scratching of the cell.

## 10. Calculation of Results.

10.1 For the calculation of the results, subtract the olefin area (1650 to 1625) from the total area (1650 to 1555) to get the aromatic area for the sample. Subtract any area found for mineral oil from the sample aromatic areas as a blank for the instrument system. Mineral oil is taken as zero aromatic content. Use a well-characterized diesel fuel, such as an ASTM NEG sample or other regional check fuel with multiple FIA data available to use for the upper aromatic content point for a calibration curve.

10.2 Use the following calculation:

$$\frac{\text{Sample area (Reference concentration)}}{\text{Reference area}} = \text{Sample concentration}$$

Sample area = total area 1650 to 1555 less olefin area 1650 to 1625  
Reference area = Sample area for reference fuel  
Reference concentration = well-established FIA aromatic content  
for reference fuel

## 11. Report.

11.1 Report the percent aromatics of the fuel by IR.

## 12. Precision and Bias.

12.1 The precision of this procedure for determining the aromatic hydrocarbon content of diesel fuels by infrared analysis has not yet been determined.

12.2 Repeatability. The repeatability of this procedure is currently being determined.

12.3 Reproducibility. The reproducibility of this procedure is currently being determined.

12.4 Bias. Bias has not been determined for this procedure, as there is no standard reference material of known aromatic content available for evaluation.



Date: November 7, 1990

Subject: EVALUATION OF AROMATIC ANALYSIS WITH FTIR METHOD

From/Location: S. Zoumalan

To/Location: A. J. Schubert

As part of method development for aromatic analysis in diesel fuel, we prepared several standards by diluting ASTM diesel standard containing 33% aromatics. These standards were prepared by dilution of the above ASTM with a pure grade of white oil.

#### ANALYSIS PROCEDURE

Basically, we followed the same procedure as proposed in SWRI draft letter of Mrs. Karen B. Kohl (for detailed procedure please refer to SWRI report attached in this letter).

#### Summary -- Method of Analysis

Optimal pathlength was obtained after several tests. The optimal pathlength through all the test was a transmission KBR sealed cell with 0.5 mm thickness. First, a background scan was taken from the empty cell. Cell was cleaned with Hexane, and then neat spectrum of white oil was obtained by subtraction of the white oil FTIR spectrum from the FTIR spectrum of the empty cell. For samples or standards, we followed a similar procedure and between each filling the cell was thoroughly rinsed with Hexane and a new background scan was refreshed by scanning the empty cell.

Measurements of area for aromatics stretching was determined by subtracting the integrated area of interval 1650-1555 wavenumbers from 1650-1625 wavenumbers interval while setting the baseline to zero at each interval. As a result of this, the net area as determined is the characteristic stretching of aromatic isomers.

A calibration curve was prepared with above procedure having four points: 33%, 16.5%, and 9.9% of aromatics. Measured area for each standard was plotted against the concentration, and a correlation coefficient of 0.99 was achieved.

Final test was the verification of accuracy. This measurement was conducted on the round robin samples and the following results were obtained.

<u>ROUND ROBIN ID#</u>	<u>FTIR, AROMATIC VOL%</u>	<u>FIA (VOL%)*</u>
	17.0	26.02
WX1	<3.0	2.22
WX2	11.5	20.42
WX3	4.5	8.40
WX4	8.8	15.23
WX5	19.5	22.60
WX6	15.5	21.03
WX7		

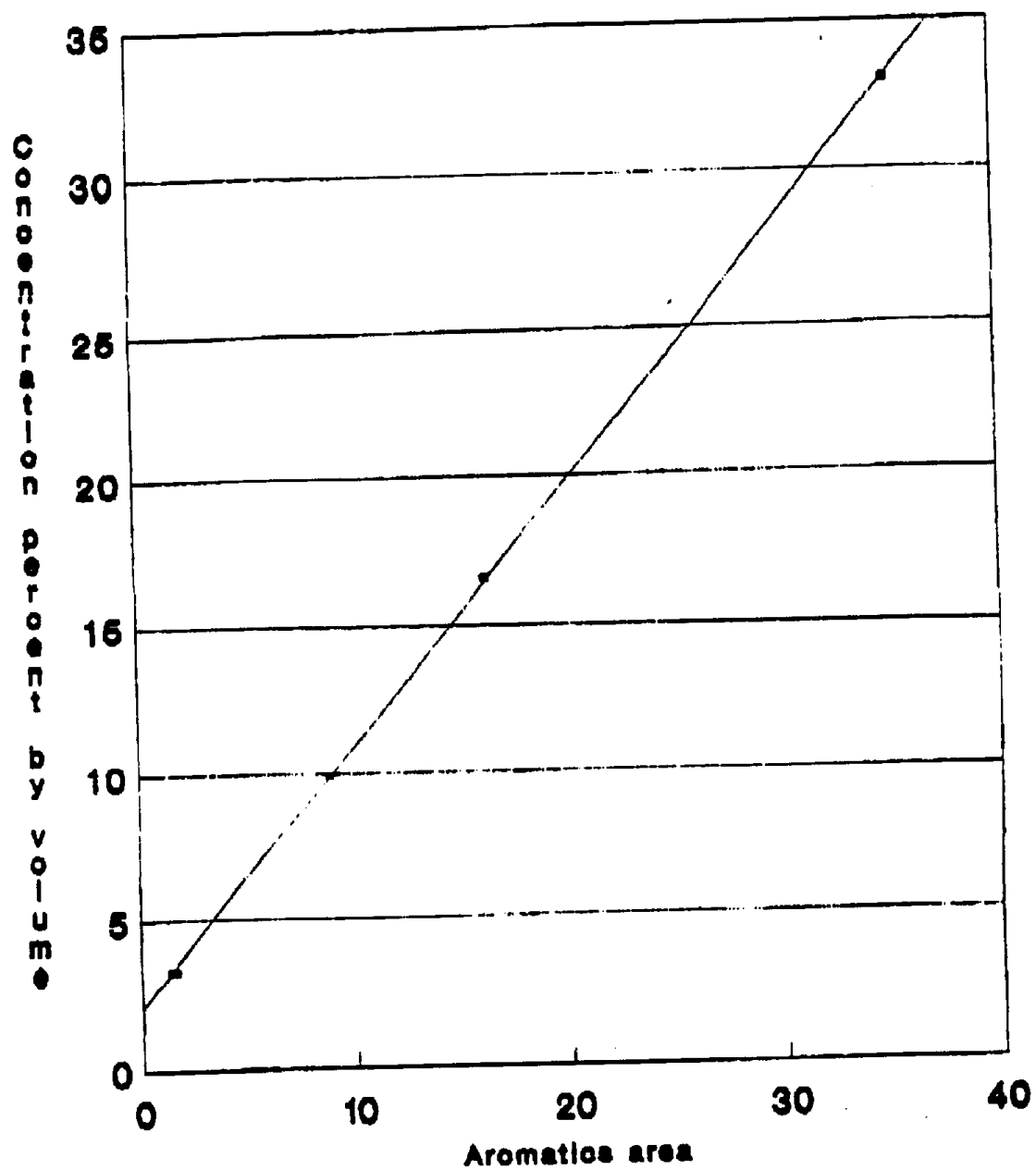
Attached with this memo, I have enclosed the calibration curve.

\* (WSPA round-robin)



# Analysis of Aromatics with FTIR

## Aromatics vs Concentration





APPENDIX C. IR PROCEDURE SENT FOR ROUND-ROBIN



# SOUTHWEST RESEARCH INSTITUTE

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March 12, 1991

Dr. John Warn M1490  
Shell Development Company  
3333 Highway Six South  
Houston, Texas 77082

Dear Dr. Warn:

I am sending you round robin samples for our program for CARB on aromatics in diesel fuels, and a copy of our draft of the new lab procedure for Aromatics in Diesel by IR. Please look it over and let me have any suggestions. We will update the calculation section as soon as we have enough valid information from pure materials to calculate our response factors. If possible, we need to have your results by March 15.

I really appreciate your performing the procedure on your instrument. There are seven diesel fuel samples ranging from about 3.5 to 35% aromatics. Please run them in triplicate and give me all the information you can on type of cell used, pathlength, instrument model, software used, and let me know what areas you obtain. The transmission method would be fine if you do not have an ATR set-up readily available. Please feel free to give me a call at (512)522-2071, or FAX (512)522-3658, if you have any questions or if I may be of some assistance.

Sincerely,

*Karen B. Kohl*

Karen B. Kohl  
Senior Research Scientist  
Petroleum Products Research  
Automotive Products and  
Emissions Research Division



SAN ANTONIO, TEXAS

HOUSTON, TEXAS • DETROIT, MICHIGAN • WASHINGTON, DC

February 18, 1991

# Standard Test Method for the Determination of the Aromatic Content of Diesel Fuels by Infrared Spectroscopy

## 1. Scope.

1.1 This test method provides for the determination of the total vol% of aromatic compounds in motor diesel fuels by infrared spectroscopy (IR) or Fourier-Transform Infrared Spectroscopy (FTIR). The range of concentration determined is from 3 to 35 volume percent.

1.2 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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4.2 Appropriate analytical methods are required in order to conform to new governmental regulations limiting aromatic content of motor diesel fuels. Both regulatory bodies and producers of diesel fuels will require similar methods for use in process and quality control.

4.3 This test method is applicable to materials in the boiling range of motor diesel fuels including dark colored materials.

4.4 Results obtained by this test method are statistically more precise than those obtained from Test Method D 1319-84, and require much shorter analysis times.

#### 5. Apparatus.

5.1 Infrared spectrophotometer or FTIR, capable of producing a computer file ready for further analysis, and capable of integrating net area between two baseline points.

#### 6. Reagents and Materials.

6.1 Isooctane - Reagent grade

6.2 Hexane or heptane - Reagent grade

6.3 Toluene - Reagent grade

#### 7. Preparation of Apparatus.

7.1 Clean the ATR cell or transmission cell before running samples and between samples with isooctane, heptane, or hexane until no oily residue from previous samples remains. If necessary, use another solvent such as toluene to insure cleanliness of the cell. Use only soft tissue to blot and gently wipe fluids from ATR crystal, if using that method.

7.2 Use manufacturer instructions regarding calibration and maintenance of instrument.

8. Procedure A, using horizontal ATR sampler.

8.1 Run a background on the infrared instrument with no sample in place, and with the cell scrupulously clean. Store background for reference use with sample spectra.

8.2 Obtain a spectrum of reagent grade isooctane over the range 1700 to 1400 and measure the area of the aromatic band at 1650 to 1550 wavenumbers, relative to the background. Set up the procedure to make the baseline effectively zero at 1650 and 1555 wavenumbers, either by setting the baseline to zero at those points, or by drawing a point to point baseline across the points and integrating the net area over the region. Do the same for the area between 1650 and 1625 to account for the olefin region of the band. Both of these areas should be zero for the isooctane. Record both of these areas for each sample.

8.3 Clean the ATR cell carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove sample film completely. Take fresh background immediately before running fuel samples. Run as for isooctane above. Repeat for each sample to be run.

9. Procedure B, using transmission cell.

9.1 Obtain a background with no sample holder in the sample chamber. New backgrounds should be acquired regularly, every hour of sample running.

9.2 Obtain a spectrum of isooctane over the range 1700 to 1400, and measure the area of the aromatic band at 1650 to 1550 wavenumbers, relative to the background. Set up the procedure to make the baseline effectively zero at 1650 and 1555 wavenumbers, either by setting the baseline to zero at those points, or by drawing a point to point baseline across the points and integrating the net area over the region. Do the same for the area between 1650 and 1625 to account for the olefin region of the band. Record both these areas for each sample.

9.3 Clean cell completely and carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove sample film completely. Obtain a spectrum of the fuel sample relative to the background. Continue the operation for the samples to be analyzed, cleaning the cell well between samples and obtaining frequent fresh backgrounds in case of staining or scratching of the cell.



## 10. Calculation of Results.

10.1 For the calculation of the results, subtract the olefin area (1650 to 1625) from the total area (1650 to 1555) to get the aromatic area for the sample. If the olefin area is negative, omit the subtraction. Subtract any area found for the isooctane from the sample aromatic areas as a blank for the instrument system. The isooctane is taken as zero aromatic content.

10.2 Use the following calculation:

Sample area = total area (1650 to 1550)  
less olefin area (1650 to 1625) \*

\*use this value only if a positive value was found

## 11. Report.

11.1 Report the aromatic area, olefin area, and sample area for each sample.

11.2 Report the manufacturer and model number of the infrared or FTIR instrument used, the type of sample cell used, and the pathlength of the cell if a transmission cell was used.



#### APPENDIX D. DATA FROM IR ROUND-ROBIN



## A-ATR

	TA	Aromatic area	REL AREA	ARO% REL	WT%RING
CRC5	1.4230	1.4221	3.863457	33.10982	16.54352
	1.4298	1.4298	3.885135	33.29560	16.63634
	1.4238	1.4238	3.868243	33.15084	16.56401
CRC8	0.3955	0.3955	0.973254	8.340791	4.167525
	0.4143	0.4143	1.026182	8.794383	4.394165
	0.4053	0.4053	1.000844	8.577238	4.285667
FL429	1.1153	1.1153	2.999718	25.70758	12.84494
	1.0996	1.0996	2.955518	25.32878	12.65567
	1.0973	1.0973	2.949042	25.27329	12.62795
FL502	0.0383	0.0383	-0.03237	-0.27746	-0.13863
	0.0548	0.0548	0.014076	0.120636	0.060276
	0.0563	0.0563	0.018299	0.156827	0.078359
CARB 5	0.2267	0.2267	0.498029	4.268110	2.132586
	0.2499	0.2499	0.563344	4.827863	2.412270
	0.2589	0.2578	0.585585	5.018468	2.507507
CARB 9	0.6995	0.6995	1.829110	15.67547	7.832344
	0.6920	0.6920	1.807995	15.49452	7.741929
	0.6462	0.6462	1.679054	14.38949	7.189795
CARB10	0.8819	0.8570	2.272522	19.47551	9.731057
	0.8774	0.8539	2.263795	19.40072	9.693686
	0.9104	0.8861	2.354448	20.17762	10.08186

B-ATR

SAMPLE	TA	Aromatic	AreaREL	AREA	aro% rel	WT%RING
FL-0429	0.9382	0.9382	3.0265		25.9367	12.9594
	0.9457	0.9457	3.0506		26.1440	13.0630
	0.9434	0.9434	3.0432		26.0804	13.0312
	0.8691	0.8691	2.8035		24.0264	12.0049
	0.8969	0.8969	2.8932		24.7949	12.3889
	0.9239	0.9239	2.9803		25.5414	12.7619
FL-0502	-0.0773	0.0000	-0.3705		-3.1752	-1.5865
	-0.0848	0.0000	-0.4065		-3.4837	-1.7407
	-0.0563	0.0000	-0.2698		-2.3122	-1.1553
CARB5	0.0773	0.0773	0.2494		2.1370	1.0678
	0.0998	0.0998	0.3219		2.7590	1.3785
	0.0353	0.0353	0.1139		0.9759	0.4876
	0.0968	0.0968	0.3123		2.6761	1.3371
	0.0653	0.0653	0.2106		1.8052	0.9020
	0.1021	0.1021	0.3294		2.8226	1.4103
CARB9	0.4999	0.4999	1.6126		13.8198	6.9052
	0.4698	0.4698	1.5155		12.9877	6.4894
	0.4728	0.4728	1.5252		13.0706	6.5308
CARB10	0.6822	0.6708	2.1639		18.5444	9.2658
	0.6815	0.6606	2.1310		18.2624	9.1249
	0.7686	0.7422	2.3942		20.5182	10.2521
CRC5	1.2857	1.2832	4.1394		35.4743	17.7249
	1.2752	1.2752	4.1135		35.2531	17.6144
	1.2774	1.2774	4.1206		35.3139	17.6448
CRC8	0.3047	0.3047	0.9829		8.4235	4.2088
	0.3070	0.3070	0.9903		8.4871	4.2406
	0.3325	0.3325	1.0726		9.1920	4.5928

C-TR

SAMPLE	TA	OA	AREA per 0.05 cell	REL AREA	aro%	WT%RING
CARB5	0.3130	0.0000	0.3130	0.404915	3.470129	1.733870
	0.3212	0.0000	0.3212	0.415523	3.561040	1.779294
	0.3227	0.0000	0.3227	0.417464	3.577670	1.787604
	0.3152	0.0000	0.3152	0.407761	3.494520	1.746057
CARB9	1.2767	0.0000	1.2767	1.651617	14.15435	7.072309
	1.2782	0.0000	1.2782	1.653557	14.17098	7.080618
	1.2647	0.0000	1.2647	1.636093	14.02131	7.005834
	1.2699	0.0000	1.2699	1.642820	14.07896	7.034640
CARB10	1.8726	0.0541	1.8185	2.352522	20.16111	10.07362
	1.8629	0.0539	1.8089	2.340103	20.05468	10.02044
	1.8471	0.0530	1.7941	2.320957	19.89060	9.938458
CRC5	3.1493	0.0000	3.1493	4.074126	34.91526	17.44561
	3.1463	0.0000	3.1463	4.070245	34.88200	17.42900
	3.1501	0.0000	3.1501	4.075161	34.92413	17.45005
CRC8	0.7731	0.0000	0.7731	1.000129	8.571108	4.282605
	0.7738	0.0000	0.7738	1.001034	8.578869	4.286482
	0.7716	0.0000	0.7716	0.998188	8.554478	4.274295
FL429	2.4956	0.0000	2.4956	3.228460	27.66790	13.82443
	2.4806	0.0000	2.4806	3.209055	27.50160	13.74134
	2.5016	0.0000	2.5016	3.236222	27.73442	13.85767
FL502	-0.0848	0.0000	-0.0848	-0.10970	-0.94015	-0.46975
	-0.0886	0.0000	-0.0886	-0.11461	-0.98227	-0.49080
	-0.0961	0.0000	-0.0961	-0.12432	-1.06542	-0.53234
	-0.0968	0.0000	-0.0968	-0.12522	-1.07319	-0.53622

D-TR

Sample		Total	Flattened Olefin	ARO AREA	REL AREA	rel aro%	WT%RING
CARB	5	0.52611	-0.00582	0.52611	0.423519	3.629561	1.813532
		0.50427	-0.00548	0.50427	0.395155	3.386485	1.692077
		0.55119	-0.00821	0.55119	0.456090	3.908699	1.953004
CARB	9	1.39269	-0.00146	1.39269	1.548948	13.27448	6.632674
		1.41632	0.00001	1.41631	1.579623	13.53737	6.764028
		1.43854	0.00143	1.43711	1.606636	13.76887	6.879699
CARB	10	2.04581	-0.07262	2.04581	2.397155	20.54362	10.26474
		2.03105	-0.07294	2.03105	2.377987	20.37934	10.18266
		2.10286	-0.07336	2.10286	2.471246	21.17858	10.58200
CRC	5	3.20658	0.00000	3.20658	3.904649	33.46284	16.71990
		3.20908	-0.02879	3.20908	3.907896	33.49066	16.73381
		3.25400	-0.03038	3.25400	3.966233	33.99062	16.98361
CRC	8	1.04135	0.00000	1.04135	1.092662	9.364116	4.678836
		0.93610	0.00000	0.93610	0.955974	8.192697	4.093529
		0.97842	0.00000	0.97842	1.010935	8.663713	4.328875
FL-0429		2.58596	0.01410	2.57186	3.080337	26.39849	13.19016
		2.61591	0.01480	2.60111	3.118324	26.72404	13.35282
		2.61314	0.01613	2.59701	3.113	26.67841	13.33002
FL-0502		0.19117	-0.00053	0.19117	-0.01146	-0.09827	-0.04910
		0.19074	-0.00042	0.19074	-0.01202	-0.10306	-0.05149
		0.23032	-0.00102	0.23032	0.039376	0.337457	0.168612



## E-ATR

Sample		Aromatic area	REL AREA	REL ARO	WT%RING
CARB	5	0.93800	0.908571	7.786457	3.890549
		0.85200	0.662857	5.680685	2.838388
CARB	9	1.30000	1.942857	16.65028	8.319413
		1.26000	1.828571	15.67085	7.830036
		1.23000	1.742857	14.93628	7.463003
CARB	10	1.34000	2.057142	17.62971	8.808791
		1.57000	2.714285	23.26142	11.62271
		1.48000	2.457142	21.05771	10.52161
CRC	5	1.97000	3.857142	33.05571	16.51648
		2.00000	3.942857	33.79028	16.88351
		1.90000	3.657142	31.34171	15.66007
CRC	8	0.96100	0.974285	8.349628	4.171941
		0.97000	1	8.57	4.282051
		1.00000	1.085714	9.304571	4.649084
FL-0429		1.73000	3.171428	27.17914	13.58021
		1.60000	2.8	23.996	11.98974
		1.70000	3.085714	26.44457	13.21318
FL-0502		0.72700	0.305714	2.619971	1.309084
		0.58200	-0.10857	-0.93045	-0.46490
		0.62000	0	0	0

F-TR

Sample		Total	Olefin	ARO AREA	REL AREA	rel aro%	WT%RING
CARB	5	4.19000	0.06800	4.12200	0.5496	4.710072	2.353415
		4.27300	0.12300	4.15000	0.553333	4.742066	2.369401
		4.00300	0.05200	3.95100	0.5268	4.514676	2.255784
CARB	9	10.88000	0.41800	10.88000	1.450666	12.43221	6.211829
		10.43700	0.14800	10.28900	1.371866	11.75689	5.874403
		12.02300	0.02900	11.99400	1.5992	13.70514	6.847856
CARB	10	11.02600	0.38800	10.63800	1.4184	12.15568	6.073661
		11.83000	0.25000	11.58000	1.544	13.23208	6.611487
		17.69100	0.19900	17.49200	2.332266	19.98752	9.986885
CRC	5	20.88500	0.16200	20.72300	2.763066	23.67948	11.83159
		26.99300	0.28800	26.70500	3.560666	30.51491	15.24695
		26.92200	0.18000	26.74200	3.5656	30.55719	15.26808
CRC	8	7.44900	0.00000	7.44900	0.9932	8.511724	4.252933
		7.64400	0.03500	7.60900	1.014533	8.694550	4.344283
		7.48000	0.01300	7.46700	0.9956	8.532292	4.263210
FL-0429		17.53300	0.08300	17.45000	2.326666	19.93953	9.962905
		17.78400	0.10400	17.68000	2.357333	20.20234	10.09422
		21.47800	0.06900	21.40900	2.854533	24.46335	12.22325
FL-0502		0.00000	0.00000	0.00000	0	0	0
		0.00000	0.00000	0.00000	0	0	0
		1.25900	0.00900	1.25000	0.166666	1.428333	0.713675

G-ATR			REL AREA	rel aro%	WT%RING
Sample		Aromatic area			
CARB	5	0.20400	0.185	1.58545	0.939057
		0.21800	0.22	1.8854	1.116717
		0.21600	0.215	1.84255	1.091337
CARB	9	0.66700	1.3425	11.50522	6.814513
		0.71600	1.465	12.55505	7.436322
		0.72900	1.4975	12.83357	7.601291
CARB	10	0.83300	1.7575	15.06177	8.921048
		0.88100	1.8775	16.09017	9.530167
		0.89100	1.9025	16.30442	9.657066
CRC	5	1.43600	3.265	27.98105	16.57310
		1.44500	3.2875	28.17387	16.68731
		1.46000	3.325	28.49525	16.87765
CRC	8	0.51700	0.9675	8.291475	4.911018
		0.53100	1.0025	8.591425	5.088677
		0.54200	1.03	8.8271	5.228267
FL-0429		1.07000	2.35	20.1395	11.92857
		1.07700	2.3675	20.28947	12.01740
		1.05200	2.305	19.75385	11.70015
FL-0502		0.12700	-0.0075	-0.06427	-0.03806
		0.13300	0.0075	0.064275	0.038069
		0.16500	0.0875	0.749875	0.444148



APPENDIX E. STATISTICAL DATA FROM IR ROUND-ROBIN



Table 1. Repeatability and Reproducibility - Relative Aromatics

<u>Fuel</u>	<u>Average Level</u>	<u>Repeatability</u>	<u>Reproducibility</u>
CARB5	3.7	0.6	1.6
CARB9	13.9	0.6	1.2
CARB10	18.8	2.0	1.9
CRC5	32.4	1.6	2.7
CRC8	8.6	0.4	0.0
FL429	24.8	1.1	2.5
FL502	-0.4	0.8	1.1

Table 2a. Average Relative Aromatics

FUEL	SDXCATR	ATR8210	TRANS	IROPT	MIDACATR	NIC0566	NICOATR	PERK
CARB5	4.70	2.20	3.53	3.64	6.73	4.66	1.77	6.41
CARB9	15.19	13.29	14.11	13.53	15.75	12.63	12.30	15.94
CARB10	19.68	19.11	20.04	20.70	20.65	15.13	15.82	20.78
CRC5	33.19	35.35	34.91	33.65	32.73	28.25	28.22	33.49
CRC8	8.57	8.70	8.57	8.74	8.74	8.58	8.57	8.57
FL429	25.44	25.42	27.63	26.60	25.87	21.54	20.06	26.37
FL502	0.00	-2.99	-1.02	0.05	0.56	0.48	0.25	0.00

Table 2b. Standard Deviations of Relative Aromatics

FUEL	SDXCATR	ATR8210	TRANS	IROPT	MIDACATR	NIC0566	NICOATR	PERK
CARB5	0.3900	0.7190	0.0517	0.2613	1.4890	0.1231	0.1622	.
CARB9	0.6961	0.4584	0.0694	0.2474	0.8599	0.9893	0.7005	.
CARB10	0.4286	1.2291	0.1363	0.4221	2.8380	4.2452	0.6643	.
CRC5	0.0976	0.1143	0.0222	0.2970	1.2565	3.9587	0.2598	.
CRC8	0.2269	0.4265	0.0125	0.5894	0.5000	0.1001	0.2685	.
FL429	0.2364	0.8456	0.1199	0.1763	1.6667	2.5394	0.2763	.
FL502	0.2410	0.6072	0.0648	0.2530	1.8410	0.8246	0.4377	.



Table 3. Repeatability and Reproducibility - Relative Area

<u>Fuel</u>	<u>Average Level</u>	<u>Repeatability</u>	<u>Reproducibility</u>
CARB5	0.4	0.1	0.2
CARB9	1.6	0.1	0.1
CARB10	2.2	0.2	0.2
CRC5	3.8	0.2	0.3
CRC8	1.0	0.0	0.0
FL429	2.9	0.1	0.3
FL502	-0.0	0.1	0.1

Table 4a. Average Relative Area

FUEL	SDXCATR	ATR8210	TRANS	IROPT	MIDACATR	NICOS66	NICOATR	PERK
CARB5	0.55	0.26	0.41	0.42	0.79	0.54	0.21	0.75
CARB9	1.77	1.55	1.65	1.58	1.84	1.47	1.44	1.86
CARB10	2.30	2.23	2.34	2.42	2.41	1.76	1.85	2.42
CRC5	3.87	4.12	4.07	3.93	3.82	3.30	3.29	3.91
CRC8	1.00	1.02	1.00	1.02	1.02	1.00	1.00	1.00
FL429	2.97	2.97	3.22	3.10	3.02	2.51	2.34	3.08
FL502	-0.00	-0.35	-0.12	0.01	0.07	0.06	0.03	0.00

Table 4b. Standard Deviations of Relative Area

FUEL	SDXCATR	ATR8210	TRANS	IROPT	MIDACATR	NICOS66	NICOATR	PERK
CARB5	0.0455	0.0839	0.0060	0.0305	0.1737	0.0144	0.0189	.
CARB9	0.0812	0.0535	0.0081	0.0289	0.1003	0.1154	0.0817	.
CARB10	0.0500	0.1434	0.0159	0.0493	0.3311	0.4954	0.0775	.
CRC5	0.0114	0.0134	0.0026	0.0347	0.1466	0.4619	0.0303	.
CRC8	0.0265	0.0498	0.0015	0.0688	0.0583	0.0117	0.0313	.
FL429	0.0276	0.0987	0.0140	0.0206	0.1945	0.2963	0.0322	.
FL502	0.0281	0.0709	0.0076	0.0295	0.2148	0.0962	0.0511	.

Table 5. Repeatability and Reproducibility - Relative Aromatics

<u>Fuel</u>	<u>Average Level</u>	<u>Repeatability</u>	<u>Reproducibility</u>
CARB1	3.2	1.6	0.0
CARB2	-0.6	0.6	1.0
CARB3	4.4	0.8	0.6
CARB4	18.0	1.0	2.8
CARB5	2.3	0.6	0.0
CARB6	20.7	1.2	2.7
CARB7	-0.9	0.3	1.6
CARB8	17.3	0.8	2.2
CARB9	12.6	0.5	0.9
CARB10	17.5	0.9	2.2
CARB11	-0.8	0.3	1.4
CARB12	23.0	0.6	3.6
CRC1	16.9	0.3	2.5
CRC5	31.6	0.1	5.2
CRC6	31.4	0.7	4.9
CRC7	32.0	1.1	4.7
CRC8	7.4	0.3	1.8
FL416	6.5	0.2	0.4
FL422	10.6	0.8	1.1
FL429	24.0	0.7	3.1
FL436	17.2	0.4	2.3
FL464	21.6	0.3	2.9
FL467	16.3	0.2	2.1
FL468	18.9	0.6	2.9
FL470	17.0	0.4	1.8
FL502	-0.6	0.2	1.1

Table 6a. Average Relative Aromatics

FUEL	SDXCATR	ATR8210
CARB1	2.30	3.37
CARB2	-1.46	0.00
CARB3	3.71	4.89
CARB4	15.49	19.60
CARB5	2.64	2.20
CARB6	18.28	22.25
CARB7	-2.27	0.00
CARB8	15.39	18.60
CARB9	11.95	13.29
CARB10	15.95	19.11
CARB11	-1.98	0.00
CARB12	19.94	25.03
CRC1	15.10	18.61
CRC5	27.95	35.35
CRC6	27.92	34.91
CRC7	28.61	35.40
CRC8	6.07	8.70
FL416	6.14	6.75
FL422	9.59	11.25
FL429	21.06	25.42
FL436	15.25	18.57
FL464	19.12	23.28
FL467	14.50	17.43
FL468	16.45	20.53
FL470	15.43	18.02
FL502	-1.60	0.00

Table 6b. Standard Deviations of Relative Aromatics

FUEL	SDXCATR	ATR8210
CARB1	0.8641	1.6247
CARB2	1.0339	0.0000
CARB3	0.1941	0.9978
CARB4	0.0333	1.2472
CARB5	0.3466	0.7190
CARB6	0.5746	1.4147
CARB7	0.4776	0.0000
CARB8	0.0273	1.0406
CARB9	0.6186	0.4584
CARB10	0.3808	1.2291
CARB11	0.5988	0.0000
CARB12	0.5139	0.6545
CRC1	0.1713	0.4437
CRC5	0.0867	0.1143
CRC6	0.5579	0.7467
CRC7	0.3411	1.4681
CRC8	0.2016	0.4265
FL416	0.0788	0.2503
FL422	0.4321	0.9144
FL429	0.2100	0.8456
FL436	0.1364	0.4512
FL464	0.1334	0.3300
FL467	0.2047	0.2194
FL468	0.3760	0.7246
FL470	0.0227	0.5084
FL502	0.2729	0.0000

Table 7. Repeatability and Reproducibility - Relative Area

<u>Fuel</u>	<u>Average Level</u>	<u>Repeatability</u>	<u>Reproducibility</u>
CARB1	0.4	0.2	0.1
CARB2	0.1	0.1	0.1
CARB3	0.6	0.1	0.1
CARB4	2.2	0.1	0.1
CARB5	0.4	0.1	0.2
CARB6	2.5	0.1	0.1
CARB7	0.0	0.0	0.0
CARB8	2.1	0.1	0.0
CARB9	1.6	0.1	0.1
CARB10	2.2	0.1	0.0
CARB11	0.0	0.0	0.0
CARB12	2.8	0.1	0.2
CRC1	2.1	0.0	0.1
CRC5	3.8	0.0	0.4
CRC6	3.8	0.1	0.3
CRC7	3.9	0.1	0.3
CRC8	1.0	0.0	0.0
FL416	0.9	0.0	0.2
FL422	1.4	0.1	0.1
FL429	2.9	0.1	0.1
FL436	2.1	0.0	0.1
FL464	2.6	0.0	0.1
FL467	2.0	0.0	0.0
FL468	2.3	0.1	0.1
FL470	2.1	0.0	0.0
FL502	0.0	0.0	0.1

Table 8a. Average Relative Area

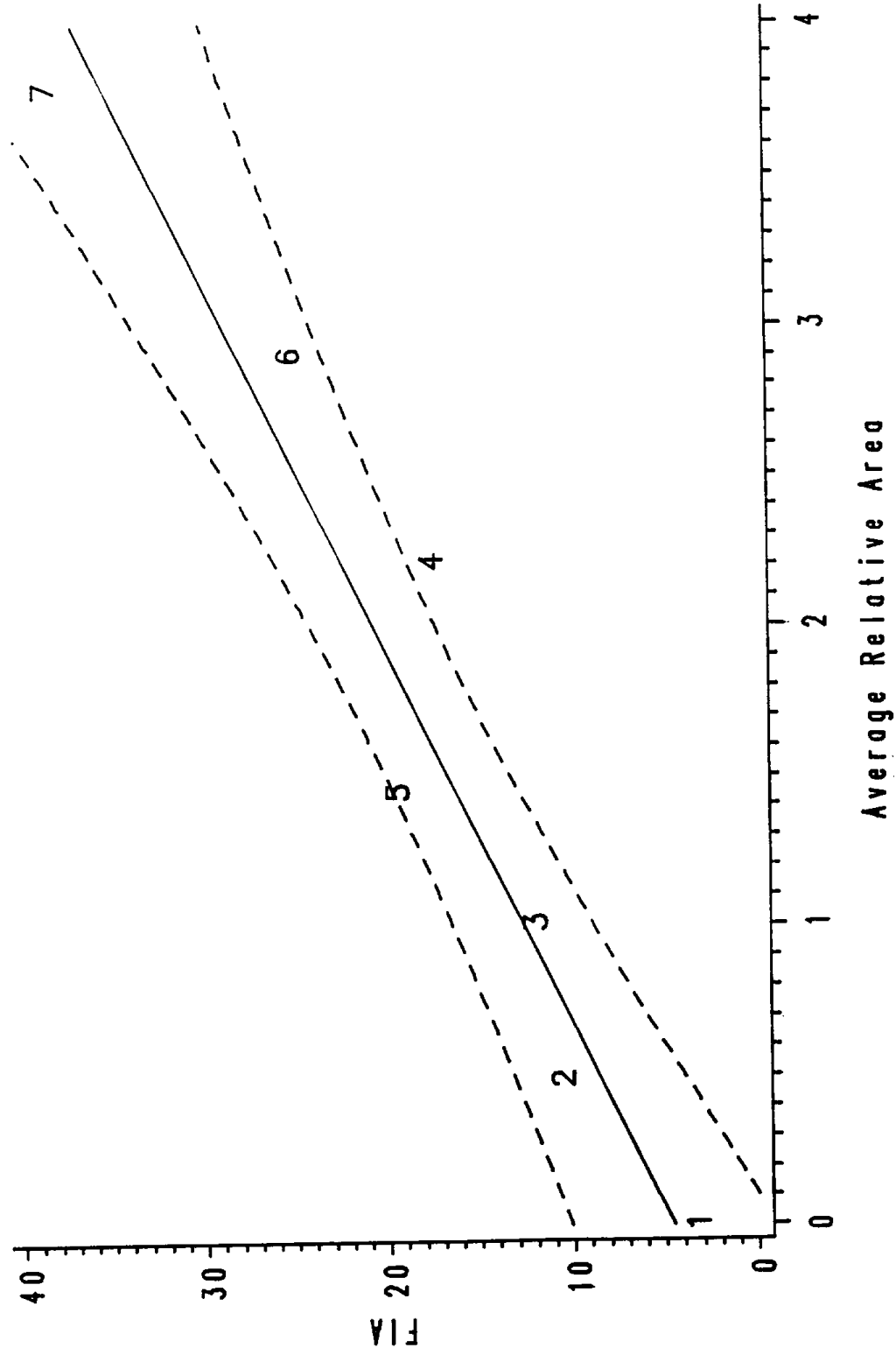
FUEL	50XCATR	ATR8210
CARB1	0.57	0.39
CARB2	0.13	0.00
CARB3	0.74	0.57
CARB4	2.11	2.29
CARB5	0.61	0.26
CARB6	2.44	2.60
CARB7	0.04	0.00
CARB8	2.10	2.17
CARB9	1.70	1.55
CARB10	2.16	2.23
CARB11	0.07	0.00
CARB12	2.63	2.92
CRC1	2.06	2.17
CRC5	3.56	4.12
CRC6	3.56	4.07
CRC7	3.64	4.13
CRC8	1.01	1.02
FL416	1.02	0.79
FL422	1.42	1.31
FL429	2.76	2.97
FL436	2.08	2.17
FL464	2.53	2.72
FL467	1.99	2.03
FL468	2.22	2.40
FL470	2.10	2.10
FL502	0.12	0.00

Table 8b. Standard Deviations of Relative Area

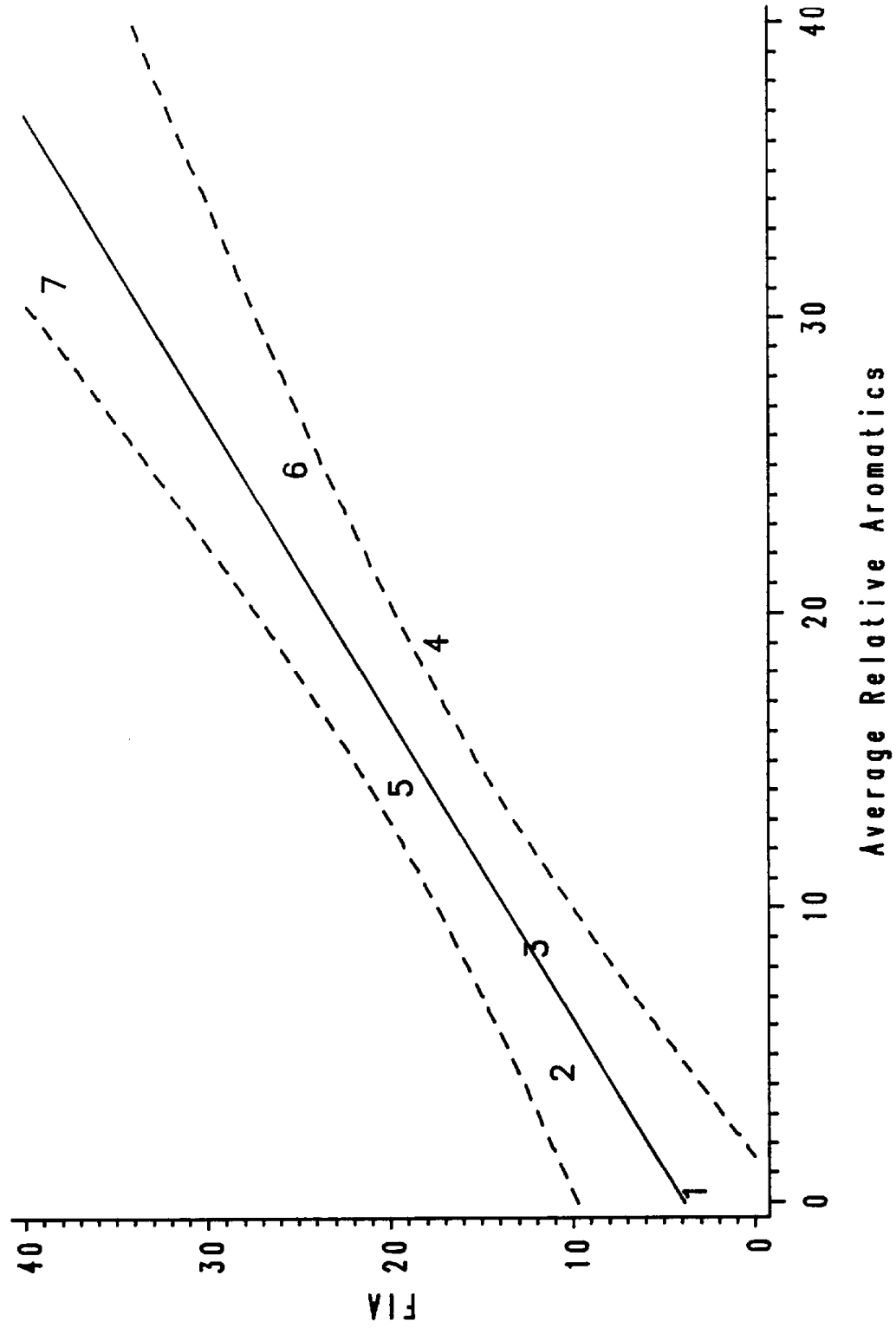
FUEL	5DXCATR	ATR8210
CARB1	0.1008	0.1896
CARB2	0.1206	0.0000
CARB3	0.0226	0.1164
CARB4	0.0039	0.1455
CARB5	0.0404	0.0839
CARB6	0.0670	0.1651
CARB7	0.0557	0.0000
CARB8	0.0032	0.1214
CARB9	0.0721	0.0535
CARB10	0.0444	0.1434
CARB11	0.0698	0.0000
CARB12	0.0599	0.0764
CRC1	0.0200	0.0518
CRC5	0.0101	0.0133
CRC6	0.0651	0.0871
CRC7	0.0398	0.1713
CRC8	0.0235	0.0498
FL416	0.0092	0.0292
FL422	0.0504	0.1067
FL429	0.0245	0.0987
FL436	0.0159	0.0526
FL464	0.0156	0.0385
FL467	0.0239	0.0256
FL468	0.0438	0.0846
FL470	0.0027	0.0593
FL502	0.0318	0.0000



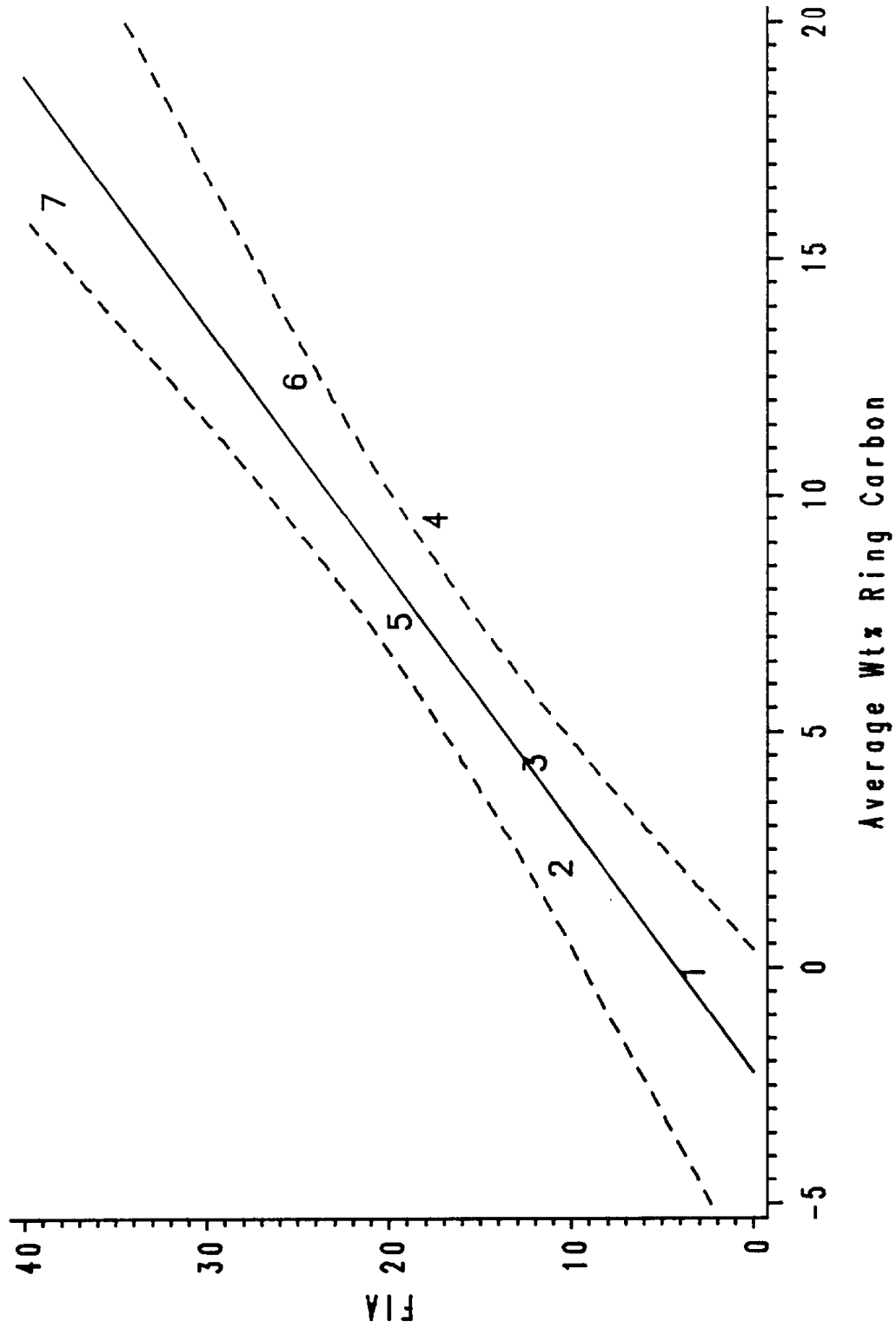
# IR Method



# IR Method



# IR Method





APPENDIX F. UV PROCEDURE SENT FOR UV ROUND-ROBIN



# SOUTHWEST RESEARCH INSTITUTE

6220 CULEBRA ROAD • POST OFFICE DRAWER 28510 • SAN ANTONIO, TEXAS, USA 78228-0510 • (512) 664-5111 • TELEX 244846

ENGINE, FUEL, AND VEHICLE RESEARCH DIVISION  
TELECOPIER: 512/622-2019

March 8, 1991

Southwest Research Institute  
Engine, Fuel, and Vehicle Research Division  
6220 Culebra Road  
San Antonio, Texas 78228-0510  
Attention: Rose Robledo, x2024

Subject: Round Robin Laboratory Evaluation of UV Method for Determination of Aromatics  
Content in California Diesel Fuels

Dear Ms. Robledo:

Thank you for your willingness to participate in the subject round robin evaluation. The California Air Resources Board would like to identify an improved method for monitoring the aromatics content in California diesel fuels. The subject method, which uses UV spectrophotometry, has been proposed as a quick reliable procedure to replace the currently used ASTM D 1319 FIA method. This method uses three wavelength regions to determine the single-, double-, and three-ring aromatic carbon composition of the fuel.

To make your efforts as easy as possible, we have enclosed the following materials:

1. Seven samples
2. Seven prewashed dilution vials
3. Dilution solvent (Optima grade isooctane)
4. Procedure description and instructions
5. Report form

You may also have received a 0.1mm UV quartz cell unless you have indicated that you have this type of cell already in your laboratory.

To allow a consistent comparison between laboratories, please follow the enclosed instructions as closely as possible. We would appreciate your report returned one week from receipt of samples. The data you return will be reduced by solving a three by three matrix of the absorbance data and compared to five other laboratories conducting the same procedure. You will be given the final comparative results and the matrix equation following completion of the round robin testing.

If you are using a scanning instrument, please return a copy of the spectra collected for each sample with your report form.

Once again, thanks for your participation in this important area of study.

Yours truly,

*Original signed by*

Brent K. Bailey  
Senior Research Engineer  
Chemical Laboratory & Fuel Processing



SAN ANTONIO, TEXAS

HOUSTON, TEXAS • DETROIT, MICHIGAN • WASHINGTON, DC

## **READ DIRECTIONS COMPLETELY BEFORE BEGINNING PROCEDURE**

Enclosed are the seven samples for round robin testing.

### **MATERIALS SUPPLIED:**

- Instructions
- 7 each, 4 dram vial samples (1 through 7)
- 7 each, 8 dram acid clean vials
- One pint, Optima iso-Octane
- Kimwipes

### **EQUIPMENT NEEDED:**

- 100 $\mu$ L glass syringe (3 1/2" needle)
- An analytical balance readable to 0.01 mg
- 20.00 mL class A volumetric pipette (acid-washed, DI water rinsed, and dried).
- A cell washer with optional nitrogen drying system (glass and teflon components only).
- Lint free lens paper
- Cell: UV quality silica, fused quartz (Suprasil or Spectrosoil) cell, 0.01 cm path.
- Glass wash bottle for solvent (acid-washed, DI water rinsed, and dried)

## **SYRINGE CLEANING**

Wash syringe with the Optima iso-Octane only.  
Rinse the syringe body several times using suction.  
Rinse plunger and needle with iso-Octane.

## **PROCEDURE FOR ANALYZING SAMPLES**

### **SINGLE BEAM INSTRUMENTS**

1. Using cell washer, rinse cell thoroughly with iso-Octane provided.
2. Allow cell to dry completely. (Must be totally dry).
3. Fill cell with iso-Octane, and read as the blank (before running samples, be sure the instrument has had sufficient time to warm-up). Rerun blank hourly.
4. Rinse cell and dry.
5. Fill cell with sample solution. If solvent is spilled on the outside of cell, wipe with solvent-wetted lint free paper. Be sure that the cell window is free of lint. Read absorbance and record values.
6. Thoroughly rinse cell with iso-Octane. Allow cell to dry completely.
7. Fill cell with next sample.



## DUAL BEAM INSTRUMENTS

1. Using cell washer, rinse cell thoroughly with iso-Octane.
2. Allow cells to dry completely. (Must be totally dry).
3. Fill one cell with iso-Octane, and the other cell with sample. If solvent is spilled on the outside of the cell, wipe with solvent-wetted lint free paper. Be sure that the cell window is free of lint. Read sample and record values.
4. Thoroughly rinse sample cell. Allow to dry completely.

## SAMPLE PREPARATION

1. Calibrate balance before use.
2. Tare the 8 dram vial with cap.
3. Samples 1 through 5; carefully draw approximately 100  $\mu$ Ls of sample into the syringe (measured volume weighs approximately 80 mgs).  
  
Samples 6 through 7; carefully draw approximately 50 $\mu$ Ls of sample into the syringe (measured volume weighs approximately 40 mgs).

4. Gently wipe the tip of the needle with a Kimwipe.
5. Inject sample in the center of the bottom of the 8 dram vial.
6. Quickly close vial, and place on balance.
7. Allow weight to stabilize. Record the sample weight in mg.
8. Immediately pipette 20.00 mLs of iso-Octane.

Hold the vial at a 20 to 30 degree angle, so that iso-Octane flows against the top of the vial wall, but do not let the tip of the pipette touch the vial wall.

9. Allow 20 to 30 seconds for the pipette to drain, and quickly touch the vial wall with the tip of the pipette.
10. Close vial and gently swirl for 10 seconds.
11. **DO NOT SHAKE! AVOID WETTING THE VIAL CAP WITH SOLUTION!  
DO NOT INVERT!**

(Hint: designate each cell as either sample or reference, and use the same cell for reference throughout this testing).

**UV AROMATICS IN CALIFORNIA DIESEL FUELS  
REPORT FORM**

<b>LABORATORY NAME &amp; ADDRESS</b>				<b>OPERATOR NAME &amp; PHONE</b>	
<b>INSTRUMENT MAKE &amp; MODEL</b>				<b>BEAM: SINGLE __ DOUBLE __</b>	
				<b>CELLTYPE:</b>	
				<b>MAX ABS 190-200nm</b>	
<b>SAMPLE NO.</b>	<b>SAMPLE WEIGHT MG/20ML</b>	<b>nm</b>	<b>ABS</b>	<b>ABS 227nm</b>	<b>ABS 255nm</b>
BLANK 1					
SAMPLE 1					
SAMPLE 2					
SAMPLE 3					
SAMPLE 4					
SAMPLE 5					
SAMPLE 6					
SAMPLE 7					
BLANK 2					
<b>COMMENTS:</b>					
<b>PLEASE RETURN THIS FORM TO BRENT BAILEY, SOUTHWEST RESEARCH INSTITUTE, SAN ANTONIO, TX 78228-0510 (512) 522-5720(FAX)</b>					

APPENDIX G. DATA AND STATISTICAL DATA FROM UV ROUND-ROBIN



Table 1. Repeatability and Reproducibility  
190 - 200nm Absorption

<u>Fuel</u>	<u>Average Level</u>	<u>Repeatability</u>	<u>Reproducibility</u>
SAMPLE 1	3.5E-03	2.7E-04	5.7E-04
SAMPLE 2	6.9E-03	3.2E-04	5.8E-04
SAMPLE 3	1.1E-02	4.0E-04	1.6E-03
SAMPLE 4	1.0E-02	2.8E-04	8.8E-04
SAMPLE 5	1.3E-02	4.5E-04	1.8E-03
SAMPLE 6	2.7E-02	6.0E-04	5.4E-03
SAMPLE 7	2.5E-02	7.7E-04	4.1E-03

Table 2a. Average 190 - 200nm Absorption

FUEL	A	B	C	D	E	F
SAMPLE 1	2.8E-03	3.9E-03	3.3E-03	4.5E-03	3.3E-03	3.2E-03
SAMPLE 2	5.7E-03	7.0E-03	7.2E-03	7.2E-03	7.3E-03	7.1E-03
SAMPLE 3	7.9E-03	1.1E-02	1.1E-02	1.3E-02	1.2E-02	1.1E-02
SAMPLE 4	8.3E-03	9.8E-03	1.0E-02	1.1E-02	1.1E-02	1.0E-02
SAMPLE 5	9.3E-03	1.2E-02	1.3E-02	1.5E-02	1.4E-02	1.3E-02
SAMPLE 6	1.6E-02	2.8E-02	2.8E-02	3.1E-02	2.9E-02	2.8E-02
SAMPLE 7	1.7E-02	2.6E-02	2.6E-02	2.9E-02	2.8E-02	2.7E-02

Table 2b. Standard Deviations of 190 - 200nm Absorption

FUEL	A	B	C	D <sup>1</sup>	E	F
SAMPLE 1	7.5E-05	2.5E-05	4.5E-05	2.2E-04	6.2E-04	5.9E-06
SAMPLE 2	1.4E-05	1.5E-05	2.5E-05	5.3E-04	5.6E-04	3.8E-06
SAMPLE 3	2.6E-05	4.4E-05	5.7E-05	7.8E-04	6.0E-04	3.7E-05
SAMPLE 4	2.4E-05	2.5E-05	3.0E-05	3.2E-04	6.0E-04	3.3E-05
SAMPLE 5	2.3E-05	3.9E-05	7.0E-05	9.4E-04	5.8E-04	4.7E-05
SAMPLE 6	1.7E-05	7.0E-05	3.9E-04	6.6E-04	1.3E-03	1.2E-04
SAMPLE 7	1.2E-05	4.9E-05	3.3E-04	1.5E-03	1.1E-03	2.1E-04

Table 3. Repeatability and Reproducibility  
227nm Absorption

<u>Fuel</u>	<u>Average Level</u>	<u>Repeatability</u>	<u>Reproducibility</u>
SAMPLE 1	6.3E-04	1.7E-05	4.7E-04
SAMPLE 2	6.7E-04	2.7E-05	8.5E-05
SAMPLE 3	1.1E-03	4.3E-05	1.1E-04
SAMPLE 4	1.1E-02	2.5E-04	5.9E-04
SAMPLE 5	3.5E-03	1.3E-04	3.5E-04
SAMPLE 6	7.4E-03	1.5E-04	5.5E-04
SAMPLE 7	1.1E-02	5.2E-04	8.1E-04

Table 4a. Average 227nm Absorption

FUEL	A	B	C	D	E	F
SAMPLE 1	4.3E-04	4.8E-04	5.1E-04	1.6E-03	4.3E-04	3.7E-04
SAMPLE 2	7.4E-04	6.5E-04	7.7E-04	5.8E-04	6.7E-04	6.2E-04
SAMPLE 3	1.0E-03	1.0E-03	1.3E-03	1.1E-03	1.1E-03	1.0E-03
SAMPLE 4	1.1E-02	1.1E-02	1.1E-02	1.2E-02	1.2E-02	1.1E-02
SAMPLE 5	3.4E-03	3.1E-03	3.5E-03	4.1E-03	3.5E-03	3.3E-03
SAMPLE 6	7.1E-03	7.0E-03	8.2E-03	7.9E-03	7.4E-03	6.9E-03
SAMPLE 7	1.1E-02	1.1E-02	1.1E-02	1.2E-02	1.2E-02	1.1E-02

Table 4b. Standard Deviations of 227nm Absorption

FUEL	A	B	C	D	E	F
SAMPLE 1	2.2E-05	3.5E-06	1.9E-05	2.4E-05	1.9E-05	1.7E-06
SAMPLE 2	6.0E-05	5.1E-06	6.4E-06	2.5E-05	1.2E-05	5.8E-07
SAMPLE 3	2.6E-05	1.1E-05	2.6E-06	1.0E-04	1.4E-05	1.3E-05
SAMPLE 4	2.7E-05	2.9E-05	1.8E-05	6.0E-04	5.0E-05	1.9E-05
SAMPLE 5	3.3E-05	2.0E-05	5.8E-07	3.2E-04	1.8E-05	4.4E-06
SAMPLE 6	7.9E-05	1.3E-05	2.4E-05	3.4E-04	4.3E-05	4.8E-05
SAMPLE 7	6.8E-05	3.0E-05	4.0E-05	1.3E-03	5.1E-05	5.7E-05



Table 5. Repeatability and Reproducibility  
255nm Absorption

<u>Fuel</u>	<u>Average Level</u>	<u>Repeatability</u>	<u>Reproducibility</u>
SAMPLE 1	2.5E-04	2.3E-05	5.7E-04
SAMPLE 2	8.2E-05	6.9E-06	5.8E-05
SAMPLE 3	1.1E-04	8.1E-06	5.8E-05
SAMPLE 4	1.7E-03	2.8E-05	9.9E-05
SAMPLE 5	5.3E-04	4.3E-05	1.7E-04
SAMPLE 6	6.4E-04	4.8E-05	1.7E-04
SAMPLE 7	2.1E-03	1.9E-03	8.9E-04

Table 6a. Average 255nm Absorption

FUEL	A	B	C	D	E	F
SAMPLE 1	1.7E-05	3.5E-05	6.7E-06	1.4E-03	3.1E-05	8.3E-06
SAMPLE 2	1.5E-04	6.2E-05	5.0E-06	1.8E-04	4.7E-05	4.0E-05
SAMPLE 3	8.5E-05	1.2E-04	5.8E-05	2.4E-04	1.2E-04	8.1E-05
SAMPLE 4	1.7E-03	1.6E-03	1.7E-03	1.9E-03	1.8E-03	1.6E-03
SAMPLE 5	4.8E-04	4.4E-04	4.3E-04	8.8E-04	4.9E-04	4.6E-04
SAMPLE 6	5.6E-04	5.7E-04	4.7E-04	9.6E-04	6.4E-04	6.3E-04
SAMPLE 7	1.5E-03	1.5E-03	1.5E-03	5.0E-03	1.7E-03	1.6E-03

Table 6b. Standard Deviations of 255nm Absorption

FUEL	A	B	C	D	E	F
SAMPLE 1	1.2E-05	0.0E+00	1.5E-05	5.0E-05	1.6E-05	5.8E-07
SAMPLE 2	6.8E-06	2.5E-06	6.0E-06	1.3E-05	6.0E-06	5.8E-07
SAMPLE 3	5.8E-06	7.1E-06	3.8E-06	1.4E-05	9.2E-06	4.0E-06
SAMPLE 4	1.7E-05	1.1E-05	3.0E-06	6.0E-05	2.3E-05	6.5E-06
SAMPLE 5	2.3E-05	3.1E-05	2.3E-06	9.6E-05	9.8E-06	2.1E-06
SAMPLE 6	2.5E-05	1.6E-05	2.9E-06	1.1E-04	2.1E-05	3.0E-05
SAMPLE 7	1.2E-05	3.8E-06	5.6E-06	4.6E-03	1.8E-05	2.7E-05

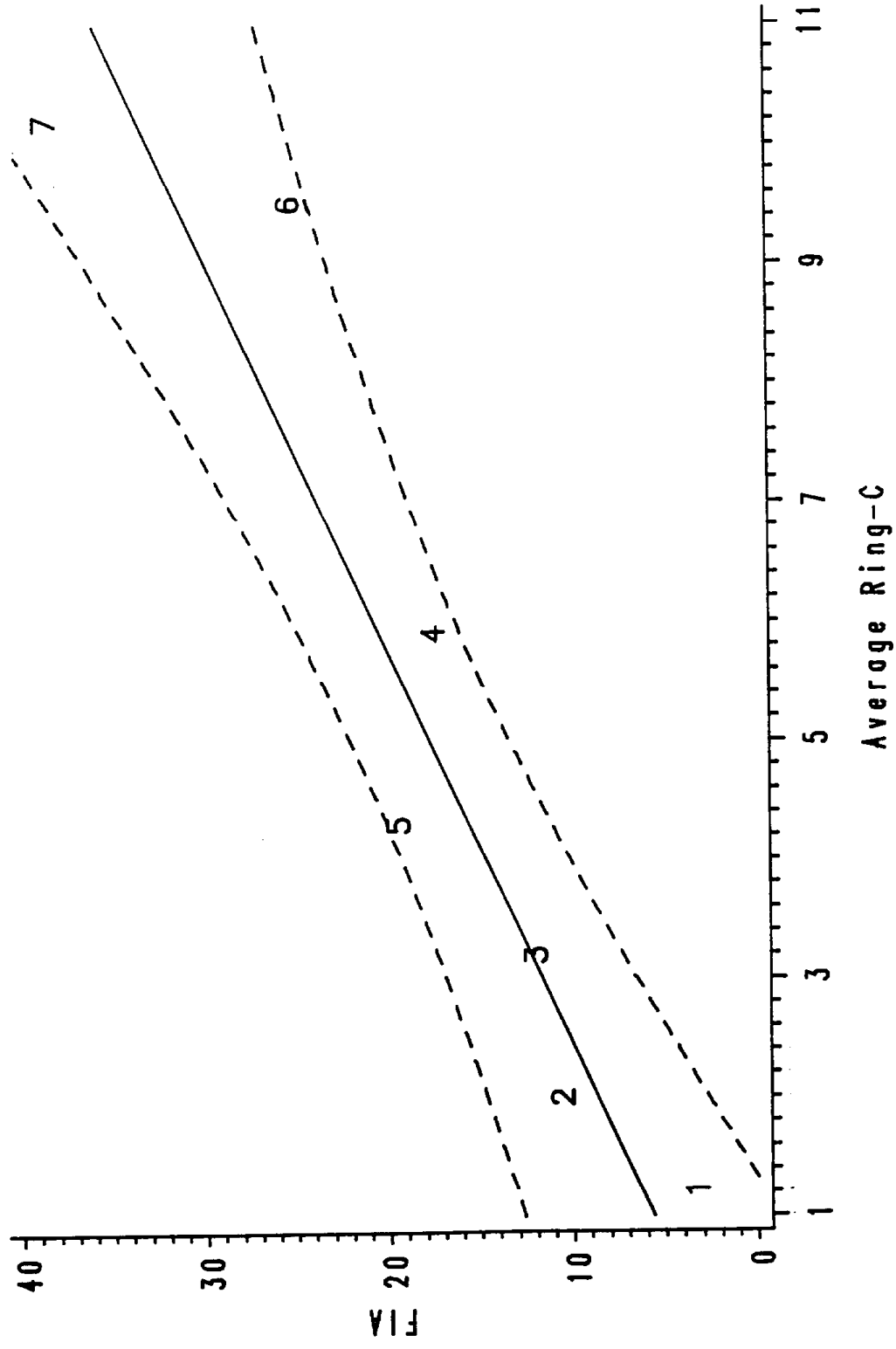
TABLE 7: REPEATABILITY AND REPRODUCIBILITY - UV  
(Standard Deviations in weight % ring carbon)

<u>FUEL</u>	<u>AVERAGE LEVEL</u>	<u>REPEATABILITY</u>	<u>REPRODUCIBILITY</u>
#1	1.2	0.02	0.59
CARB5	2.0	0.05	0.26
CRC8	3.2	0.10	0.38
CARB10	5.9	0.12	0.48
CARB9	4.3	0.14	0.52
FL429	9.5	0.09	0.85
CRC5	10.2	0.55	1.56

TABLE 8. AVERAGE TOTAL AROMATICS CONTENT - UV  
(wt% ring carbon)

<u>Fuel</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>FIA</u>
#1	0.9	1.0	1.0	1.1	2.5	1.0	3.4
#2	1.8	1.8	2.0	2.1	2.5	2.0	11.4
#3	2.4	3.0	3.2	3.4	4.0	3.2	12.6
#4	5.6	4.7	6.1	6.5	6.8	6.0	18.2
#5	3.4	3.6	4.4	4.5	5.5	4.2	19.5
#6	6.2	11.5	9.2	9.6	11.0	9.2	25.5
#7	7.8	10.1	9.9	10.7	12.9	10.1	40.2

# UV Method



APPENDIX H. FINAL DRAFTS OF IR AND UV PROCEDURES



June 6, 1991

## Standard Test Method for the Determination of the Aromatic Content of Diesel Fuels by Infrared Spectroscopy

### 1. Scope.

1.1 This test method provides for the determination of the total vol% of aromatic compounds in motor diesel fuels by infrared spectroscopy (IR) or Fourier-Transform Infrared Spectroscopy (FTIR). The range of concentration determined is from 5 to 40 volume percent.

1.2 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

### 2. Referenced Documents.

#### 2.1 ASTM Standards

D 1319 Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

E 168-67 Standard Recommended Practices for General Techniques of Infrared Quantitative Analysis

### 3. Summary of Test Method.

3.1 A small amount of fuel is introduced into a transmission cell of known path length, or placed on a horizontal attenuated total reflectance (ATR) sampler, and an infrared spectrum obtained using either infrared or FTIR, to include the area from 1700 to 1400 wavenumbers. The area between 1650 and 1550 is integrated, and the area related to the aromatics content of the diesel fuel.

#### 4. Significance and Use.

4.1 The aromatic hydrocarbon content of middle distillate fuels (diesel, jet, heating oil) is a significant factor in their combustion properties.

4.2 Appropriate analytical methods are required in order to conform to new governmental regulations limiting aromatic content of motor diesel fuels. Both regulatory bodies and producers of diesel fuels will require similar methods for use in process and quality control.

4.3 This test method is applicable to materials in the boiling range of motor diesel fuels including dark colored materials.

4.4 Results obtained by this test method are statistically more precise than those obtained from Test Method D 1319-84, and require much shorter analysis times.

#### 5. Apparatus.

5.1 Infrared spectrophotometer or FTIR, capable of producing a computer file ready for further analysis, and capable of integrating net area between two baseline points.

5.1 BaF<sub>2</sub> or CaF<sub>2</sub> fixed pathlength cell, 0.1 to 0.5 pathlength, or Horizontal ATR sampling attachment for FTIR with Ge or equivalent crystal.

#### 6. Reagents and Materials.

6.1 Isooctane - Reagent grade

6.2 Hexane or heptane - Reagent grade

6.3 Toluene - Reagent grade

6.4 Mineral Oil - Pharmaceutical Grade

6.5 Standardization solution - 5.00 grams toluene made to 50.00 grams with mineral oil. Mix thoroughly. Store in tightly sealed container and keep from light.



## 7. Preparation of Apparatus.

7.1 Clean the ATR cell or transmission cell before running samples and between samples with isooctane, heptane, or hexane until no oily residue from previous samples remains. If necessary, use another solvent such as toluene to insure cleanliness of the cell. Use only soft tissue to blot and gently wipe fluids from ATR crystal, if used.

7.2 Use manufacturer instructions regarding calibration and maintenance of instrument.

## 8. Procedure A, using horizontal ATR sampler.

8.1 Run a background on the infrared instrument with no sample in place, and with the cell scrupulously clean. Store background for reference use with sample spectra.

8.2 Obtain a spectrum of reagent grade isooctane over the range 1700 to 1400 and measure the area of the aromatic band at 1650 to 1550 wavenumbers, relative to the background. Set up the procedure to make the baseline effectively zero at the point of minimum absorbance near 1650 and 1555 wavenumbers, either by setting the baseline to zero at those points, or by drawing a point to point baseline across the points and integrating the net area over the region. Do the same for the area between 1650 and 1625 to account for the olefin region of the band. Both of these areas should be zero for the isooctane. Record both of these areas for each sample.

8.3 Run standarization solution as described above for isooctaine. Clean the ATR cell carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove film completely. Take fresh background immediately before running samples. Run as for isooctane above. Record areas for use in relative area calculation.

8.4 Clean the ATR cell carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove sample film completely. Take fresh background immediately before running fuel samples. Run as for isooctane above. Repeat for each sample to be run. Record areas.

## 9. Procedure B, using transmission cell.

9.1 Obtain a background with no sample holder in the sample chamber. New backgrounds should be acquired regularly, every hour of sample running.

9.2 Obtain a spectrum of isooctane over the range 1700 to 1400, and measure the area of the aromatic band at 1650 to 1550 wavenumbers, relative to the background. Set up the procedure to make the baseline effectively zero at the points of minimum absorbance near 1650 and 1555 wavenumbers, either by setting the baseline to zero at those points, or by drawing a point to point baseline across the points and integrating the net area over the region. Do the same for the area between 1650 and 1625 to account for the olefin region of the band. Record both these areas for each sample.

9.3 Run standardization solution in the same manner. Clean the cell carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove film completely. Dry cell well. Take fresh background immediately before running samples. Run as for isooctane above. Record areas for use in relative area calculation.

9.3 Clean cell completely and carefully with isooctane, hexane or heptane, repeating with toluene if necessary to remove sample film completely. Be sure to dry cell well with dry air or nitrogen. Obtain a spectrum of the fuel sample relative to the background. Continue the operation for the samples to be analyzed, cleaning the cell well between samples and obtaining frequent fresh backgrounds in case of staining or scratching of the cell.

## 10. Calculation of Results.

10.1 For the calculation of the results, first subtract any area found for the isooctane from the sample aromatic areas as a blank for the instrument system. The isooctane is taken as zero aromatic content. Using the corrected area values, subtract the olefin area (1650 to 1625) from the total area (1650 to 1555) to get the aromatic area for the sample. If the olefin area is negative, omit the subtraction.

10.2 Use the following calculation:

$$\text{Sample area} = \text{corrected total area (1650 to 1550)} \\ \text{less olefin area (1650 to 1625)*}$$

\*use this value only if a positive value was found

10.3 Use the following equations to obtain relative aromatic area:

$$\text{Sample area/standardization solution area} = \\ \text{relative aromatic area}$$

10.4 Use one of the following equations to obtain either relative volume % aromatic content (predictive of FIA-type value) or weight % ring carbon content (predictive of NMR value)

Relative aromatic area x 16.5 = predicted vol% aromatics

Relative aromatic area x 8.37 = predicted wt% ring carbon

#### 11. Report.

11.1 Report the predicted aromatic content, or the predicted wt% ring carbon value for each sample, noting the value reported.



Standard Test Method for the Determination of the Aromatic Content  
of Diesel Fuels by Ultraviolet Spectroscopy

1. Scope.

1.1 This test method provides for the determination of the weight percent of mono-, di-, and tri-ring aromatic compounds in motor diesel fuels by ultraviolet spectroscopy (UV). The range of concentration determined is from 1 to 40 weight percent.

1.2 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents.

2.1 ASTM Standards

D 1319 Hydrocarbon Types in Liquid Petroleum Products by  
Fluorescent Indicator Adsorption

3. Summary of Test Method.

3.1 A small amount of fuel is diluted in iso-octane, then introduced into a transmission cell of 0.01cm fixed path length. The absorbance is measured at three wavelengths, compared with extinction coefficients of standard materials using a calculation, and reported in weight percent of the various aromatic structures.

#### 4. Significance and Use.

4.1 The aromatic hydrocarbon content and aromatic structure of middle distillate fuels (diesel, jet, heating oil) are significant factors in their combustion properties.

4.2 Appropriate analytical methods are required in order to conform to new governmental regulations limiting aromatic content of motor diesel fuels. Both regulatory bodies and producers of diesel fuels will require similar methods for use in process and quality control.

4.3 This test method is applicable to materials in the boiling range of motor diesel fuels including dark colored materials.

4.4 Results obtained by this test method are statistically more precise than those obtained from Test Method D 1319-84, and require shorter analysis times.

#### 5. Apparatus.

5.1 Ultraviolet spectrophotometer, single or dual beam, capable of producing a computer file ready for further analysis, or of producing a chart output.

5.2 Cell: UV quality silica, fused quartz (Suprasil or Spectrosil), 0.01cm pathlength.

5.3 Balance, capable of weighing to four places.

#### 6. Reagents and Materials.

6.1 Iso-octane - Reagent grade (Optima)

6.2 Volumetric flasks, 25 mL, with caps, acid cleaned (with NOCHROMIX)

6.3 50 and 100 microliter glass syringes

6.4 Cell washer system made up of a vacuum flask trap with an eyedropper suction tip.

6.5 Lint-free lens paper

6.6 Glass wash bottle for solvent

## 7. Preparation of Sample.

7.1 Clean the syringe with the high purity iso-octane only. Rinse the syringe body several times using suction. Rinse plunger and needle with iso-octane. If density is known, proceed to step 7.3.

7.2 Calibrate balance before use; tare 25 mL volumetric flask with cap.

7.3 Carefully draw into the syringe exactly the volume required. For dark diesel use 20 microliters; for light diesel use 100 microliters.

7.4 Gently wipe the tip of the needle with a tissue, taking care not to allow sample to wick into the tissue.

7.5 Inject sample into the center of the bottom of the volumetric. Quickly close with cap. If density is known, proceed to step 7.7.

7.6 Place volumetric on balance. Allow weight to stabilize. Record sample weight in mg.

7.7 Immediately pipette iso-octane into the volumetric flask, filling to the proper 25 mL volume level. Close flask and invert several times to insure a homogenous solution.

## 8. Procedure A, using single beam instrument. sampler.

8.1 Using cell washer for solvent removal and drying, rinse cell thoroughly with iso-octane. Allow cell to dry completely. (Must be totally dry).

8.2 Fill cell with iso-octane, and read as the blank (before running samples, be sure the instrument has had sufficient time to warm up). Rerun blank hourly.

8.3 Rinse cell and dry. Fill cell with sample solution. If solvent is spilled on the outside of cell, wipe with solvent-wetted lint free lens paper. Be sure that the cell window is free of lint. Scan sample from 290nm to 190nm. Read absorbance at 255nm, 227nm, and the maximum absorbance in the 196 to 190nm range. Absorbance values should be between 0.2 and 2.0. If out of range, sample should be remade using a larger or smaller microliter amount of fuel to get in range. (If instrument has not been in use for one hour, run another blank).

8.4 Thoroughly rinse cell with iso-octane. Allow cell to dry completely. Fill cell with next sample.

9. Procedure B, using double beam instrument.

9.1 Using cell washer for solvent removal and drying, rinse cell thoroughly with iso-octane. Allow cell to dry completely. (Must be totally dry).

9.2 Fill one cell with iso-octane and the other cell with sample. If solvent is spilled on the outside of the cell, wipe with solvent-wetted lint free paper. Be sure that the cell window is free of lint. Scan sample from 290nm to 190nm. Read absorbance at 255nm, 227nm, and the maximum absorbance in the 196 to 190nm range. Absorbance values should be between 0.2 and 2.0. If out of range, sample should be remade using a larger or smaller microliter amount of fuel to get in range. (If instrument has not been in use for one hour, run another blank).

9.3 Thoroughly rinse sample cell. Allow to dry completely. Note: designate one cell as sample, the other as reference, for use throughout testing.

10. Calculation of Results.

10.1 The calculated extinction coefficient is a three-by-three matrix, which takes into account the background area that is contributed by each of the aromatics present at each wavelength. The matrix for the aromatics is as follows:

	191 nm	227 nm	255 nm
MONO	771	12.9	7.68
DI	85.3	650	23.4
TRI	214	124	357



10.2 Equations for the weight percent values of the aromatic components are given by the equations below:

$$\begin{aligned}\text{Mono Aromatics} &= X * S * 100/W \\ \text{Di Aromatics} &= Y * S * 100/W \\ \text{Tri Aromatic} &= M * S * 100/W\end{aligned}$$

Where S = solvent mLs used to make up the sample

$$\begin{aligned}X &= (A1 - R4 * Y - R7 * M) / R1 \\ Y &= (R1 * A2 - R2 * A1 + (R2 * R7 - R1 * R8) * M) / (R1 * R5 - R2 * R4) \\ M &= RO / (Z - (R1 * R6 - R3 * R4) * (R2 * R7 - R1 * R8)) \\ W &= \text{Sample volume in microliters} * \text{Density (or weight in mg)} \\ Z &= (R1 * R5 - R2 * R4) * (R3 * R7 - R1 * R9) \\ RO &= (R1 * R6 - R3 * R4) * (R1 * A2 - R2 * A1) - (R1 * R5 - R2 * R4) * (R1 * A3 - R3 * A1) \\ A1 &= \text{absorbance at MAX at 190-196 nm} * 100 \\ A2 &= \text{absorbance at 227 nm} * 100 \\ A3 &= \text{absorbance at 255 nm} * 100\end{aligned}$$

And where R1 through R9 values are: 771, 12.9, 7.68, 85.3, 650, 23.4, 214, 124, 357. (This calculation is facilitated by the use of a short computer program.) Example basic program is Appendix A.

## 11. Report.

11.1 Report the weight percent mono-, di-, and tri- ring aromatic values calculated using the equations above, and the total aromatic weight percent if requested.

# APPENDIX A - Basic Program: Aromatics on CRN LA

```

10DATA 771,12.9,7.68,85.3,650,23.4,214,124,357
15PRINT
18READ R1,R2,R3,R4,R5,R6,R7,R8,R9
20PRINT"    UV AROMATICITY"
40PRINT" THIS PROGRAM CALCULATES THE WEIGHT %"
50PRINT"ONE-,TWO-, AND THREE-RING CARBON IN"
60PRINT"MIDDLE DISTILLATE FUELS AND LUBRICATING"
70PRINT"OIL BASESTOCKS."
80PRINT
90PRINT" THE CALCULATION REQUIRES THE VOLUME &"
100PRINT"DENSITY OF THE SAMPLE (OR WEIGHT), THE"
110PRINT"VOLUME OF SOLVENT, AND THE ABSORBANCES"
120PRINT"AND THE WAVELENGTHS OF 195, 225, AND 255NM"
140PRINT
162PRINT"SAMPLE ID";
166INPUTB$
170PRINT
180PRINT"WEIGHTED SAMPLE (Y OR N)";
190INPUT N$
200PRINT
210IFN$+"N"GOSUB300
230PRINT"WEIGHT OF SAMPLE (MG)";
240INPUTW
250PRINT
260GOTO350
300PRINT"VOLUME SAMPLE, UL";
310INPUTV
320PRINT
330PRINT"DENSITY, GM/ML? ";
340INPUTD
342PRINT
345LETW=D*V
350PRINT"VOLUME SOLVENT (mL)";
360INPUTS
370PRINT
380PRINT" ABSORBANCE AT 195,225,255";
390INPUTA1,A2,A3
400PRINT
410LETR0=(R1*R6-R3*R4)*(R1*A2-R2*A1)-(R1*R5-R2*R4)*(R1*A3-R3*A1)
420LETZ+(R1*R5-R2*R4)*(R3*R7-R1*R9)
430LETM=R0/(Z-(R1*R6-R3*R4)*(R2*R7-R1*R8))
440LETY=(R1*A2-R2*A1+(R2*R7-R1*R8)*M)/(R1*R5-R2*R4)
450LETX=(A1-R4*Y-R7*M)/R1
460PRINTX,Y,M
470PRINT
480LETC1=X*S*100/W
490LETC2=Y*S*100/W
500LETC3=M*S*100/W
510PRINT"MONO % = "C1" (WT)"
520PRINT"DI  % = "C2" (WT)"
550PRINT"TRI  % = "C3" (WT)"
570PRINT
580PRINT"ANY MORE SAMPLES (Y OR N)";
590INPUTH$
600IFH$="Y"GOSUB90
620IFH$="N"GOSUB650
650PRINT
660END

```

## APPENDIX I. NIR FEASIBILITY STUDY



CARIS

# SOUTHWEST RESEARCH INSTITUTE

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FUELS AND LUBRICANTS RESEARCH DIVISION  
Fax No.: (512) 522-5720

14 January 1991

Allen N. Bickel  
National Sales & Marketing Manager  
LT Industries  
6110 Executive Blvd.  
Rockville, Maryland 20852

Subject: Diesel Fuel Samples for NIR Analysis of Aromatics

Dear Mr. Bickel:

As we discussed earlier, I am submitting the diesel fuel samples described below for analysis of the aromatic fraction by Near Infrared. The volume percent aromatic content for 25 out of the total of 30 samples as measured by ASTM Method D 1319 are given to develop a NIR model for these fuels. There are 5 samples that you may then apply the model to predict the aromatic content.

This is the maximum number of samples that we were able to send now for this application. The samples have been carefully selected to represent a wide cross section of aromatic contents in the fuel. The 5 unknown samples fall within the range of the other samples so that it will not be necessary for the model you develop from the other 25 samples to extrapolate a value beyond the region of this sample set.

The results that are needed for evaluating the NIR method is a table of model-predicted data versus actual values, and also a table of predicted values for the five unknown samples. In addition to these basic results, we are interested in any statistical analyses of the data that you might perform, such as, the root mean square error and R-square values, if this is convenient for you.

If there are any questions concerning the samples, please call me directly at 512-522-3247. Thank you for your interest and cooperation in this effort. We look forward to receiving your results at the earliest possible date.

Yours truly,

*Brent K. Bailey*

Brent K. Bailey  
Senior Research Engineer  
Chemical Laboratory and Fuel Processing

/esm



*B. K. Bailey*

SAN ANTONIO, TEXAS

HOUSTON, TEXAS • DETROIT, MICHIGAN • WASHINGTON, DC

SAMPLE SET FOR LT INDUSTRIES NIR ANALYSIS	
Sample No.	FIA Aromatics, Volume % (ASTM Method D 1319)
CRC 1	16.6
CRC 2	43.9
CRC 3	46.9
CRC 4	19.0
CRC 5	33.5
CRC 6	33.5
CRC 7	33.5
CRC 8	11.1
CRC 9	42.9
CARB 1	****
CARB 2	2.0
CARB 3	8.7
CARB 4	24.1
CARB 5	8.8
CARB 6	29.0
CARB 7	1.8
CARB 8	16.4
CARB 9	20.0
CARB 10	16.0
CARB 11	1.7
CARB 12	****
SwRI 1 (FL-0416-F)	****
SwRI 2 (FL-0422-F)	****
SwRI 3 (FL-0429-F)	****
SwRI 4 (FL-0436-F)	17.7
SwRI 5 (FL-0464-F)	17.9
SwRI 6 (FL-0467-F)	16.4
SwRI 7 (FL-0468-F)	15.0
SwRI 8 (FL-0470-F)	19.6
SwRI 9 (FL-0502-F)	2.7

7.1

23.1

15.9

11.6

20.7



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March 11, 1991

Dr. Karen B. Kohl  
Southwest Research Institute  
6220 Culebra Road  
P.O. Drawer 28510  
San Antonio, Texas 78228-0510

Dear Karen:


It was a pleasure to meet you at the Pittsburgh Conference in Chicago. I hope your short visit with us was useful in providing you with information on both LT industries, as well as Near Infrared methodology.

Enclosed please find a copy of a report of the work performed on the diesel samples that you have submitted to LT Industries for evaluation of aromatic content.

Based on the application study performed, it appears that we can measure the percent aromatics in diesel fuel quite well, both in a control lab environment, as well as on-line. Based on our discussions of the limits of the current method, I think that our results are optimized, and can even be improved with an improvement in the primary method.

If I can be of any further assistance, please contact me at (301) 468-6777.

Sincerely,

  
Lawrence P. McDermott  
Senior Applications Scientist

cc. Allen Bickel  
National Sales and Marketing Manager

Brent Bailly  
SWRI

Ken Conrad  
Intek Corporation

FEASIBILITY STUDY REPORT

SOUTHWEST RESEARCH INSTITUTE

MARCH 11, 1991

L.T. INDUSTRIES INC.



## APPLICATIONS STUDY REPORT. SOUTHWEST RESEARCH INSTITUTE.

### STUDY OBJECTIVE

To determine if the Quantum 1200 NIR analyzer can measure the percent aromatics in diesel fuel.

### EXPERIMENTAL PROCEDURES

Near Infrared spectra were obtained using the Quantum 1200 NIR Analyzer. Each sample submitted was scanned using a direct insertion probe with a 10 mm pathlength. An empty probe was used for a reference scan. Each scan sequence consisted of the average of thirty rapid scans of each sample. The scan rate of the Quantum 1200 is 2.5 complete 1200 point spectral scans from 900 to 1800 nm per second. The instrument was configured for operation in the AQUA region of the spectrum, (900-1800 nm).

Twenty five samples were submitted for calibration, and five unknowns were submitted for prediction. All spectra were collected in the transreflectance mode.

### RESULTS

Figure 1 shows scans of several of the samples scanned in the absorbance format. The spectra were treated by using an area normalization to compensate for differences due to differences in color. The predominant features seen are due to various C-H stretches, both aromatic and saturated.

Derivative transforms were applied to enhance spectral differences. Derivative transforms are useful for enhancing spectral resolution by removing baseline offsets due to effects such as particle size, color differences, and slight differences in effective pathlength. The major features seen in the NIR region are due to combinations and overtones of fundamental vibrations that occur in the traditional mid infrared region of the spectrum. Strong NIR absorbers include C-H, O-H, N-H, C=O, =C-H, COOH, and aromatic C-H groups.

Figure 2 and 3 show scans of several of the samples in the first and second derivative format. All results reported are based on using a first derivative treatment of the area normalized absorbance spectra. To develop a calibration equation for at or on-line analysis chemometric single and multiple variable analysis routines are run on a calibration set of spectra with known

concentrations. Chemometric tools included in the Spectrametrics package for routine analysis include a single wavelength linear regression, a multiple wavelength linear regression, factor analysis, and a discriminant analysis capability that is used for qualitative analysis. Principle Components Regression, and Partial Least Squares analysis algorithms are included in the optional software package LightCAL. These powerful algorithms calibrate using all of the spectral data points, as opposed to using one or several wavelengths. All of the regression algorithms are used to determine a relationship between the spectral absorbance at one, several, or all of the wavelengths and the concentration of the constituent of interest. This relationship takes the form of an equation with a coefficient at each wavelength used, and the equation is used to predict the concentration of future unknown samples.

Typical NIR calibration sets range in the number of samples from 15 through 50 samples. The number of samples required for robust calibration development will vary with the number of variables that are subject to change.

Correlation techniques such as multiple linear regression and partial least squares regression techniques were used to determine models to relate spectral response to primary values. The multiple linear regression technique typically chooses from 1 through 5 wavelengths to model on, while the PLS technique utilizes the full spectra. The choice of the optimum modeling technique is typically made after a larger sample set is evaluated for validation purposes. PLS techniques are becoming the more popular of the two techniques for method development, however multiple linear regression was also evaluated.

Calibration models developed across the full range of samples submitted using the PLS method with a complete "leave one out" cross validation obtained a standard error of prediction of 3.1 percent using a four factor model. Because only a few samples were submitted above 30 percent aromatics, a second PLS calibration was performed over the range below 30 percent. The Standard Error of Prediction obtained on cross validation within this range was 2.17 percent aromatics.

Figures 4 and 6 show the fit obtained over the full range as well as over the low range examined. Figures 5 and 7 show the regression coefficients calculated for both the full and low range calibration sets using PLS modeling. It can be seen that the regression coefficients are weighted heavily in the 1600 nm region of the spectrum which is characteristic of aromatic functional groups.

One important feature available with the Lightcal PLS software package is the ability to qualify the spectra of unknown samples while predicting them. Several diagnostics are included in this package to insure that confidence can be given in the predicted values. The calibration set is characterized by the scores calculated for each of the factors calculated in the modeling session. The scores for the "unknown" sample are also calculated,

The Mahalanobis distance is the "unit distance vector," a measure of the likelihood of a point to be a part of a group. The distance of a point from a group of points is found to matter much less along the direction of elongation of point groups than perpendicular to that direction.

and a mahalanobis distance is calculated to determine if the sample is similar to the calibration set from which the model was derived. Samples that look "different" are predicted with a warning that the predicted value may be erroneous. An example of this occurred with one of the unknowns, the sample fl-416-f. This sample was identified as having a very high mahalanobis distance, as indicated in figure 8. This sample was "flagged" indicating that our predictions may not be accurate. A plot of the scores for the calibration samples, plotted in green, as well as for the unknown sample, plotted in red, is presented in figure 9, which shows that the scores for the second and fourth factor fall outside of the domain of the calibration set, again decreasing the confidence in our predicted values.

Multiple linear regression models obtained using two wavelengths provided a standard error of calibration of 3.0 and 2.0 percent aromatics for the full and limited range calibration sets. The key wavelength chosen for each model, 1613 and 1600 nm for the full and low range calibration sets is characteristic of aromatic C-H stretches as confirmed by Colthrup tables. It is likely that the standard error of prediction for the MLR models would be slightly higher than the standard error of calibration reported.

The five unknown samples submitted were predicted using the various models developed. The predicted values are listed below.

#### SWRI CALIBRATIONS FOR AROMATICS IN DIESEL FUELS

SAMPLE ID	PLS	MLR	MLR LOW	PLS LOW
FL-429-F	26.56	27.10	21.90	21.15
CARB-1	9.12	11.25	8.60	8.26
FL-416-F	11.64	19.70	12.80	8.28 *
FL-422-F	15.00	15.90	13.50	12.30
CARB-12	23.64	24.00	20.90	21.88

\* DENOTES SAMPLE FLAGGED AS POTENTIAL OUTLIER  
BASED ON STATISTICAL ANALYSIS OF CALIBRATION SET  
AGAINST UNKNOWN SAMPLE (LTCAL PREDICTION)

\* MLR MODELS BASED ON 2 WAVELENGTH EQUATIONS  
\* PLS MODELS BASED ON 4 FACTOR MODELS AS DETERMINED  
BY COMPLETE CROSS VALIDATION

Routine analysis of these product types can be performed in the lab, at-line, or on-line. The sample analysis mode is often reduced to typing in a file name, and pressing the enter key. A loop can then repeat the analysis at the desired frequency. All math treatments, and application of the regression equation are then performed automatically, and the result is displayed on the screen, to the printer, or if desired transmitted to a process control computer for closed loop operation.

## CONCLUSIONS

The Quantum 1200 NIR analyzer is ideal for the analysis of the aromatics in diesel fuel. The high signal to noise available with the Quantum 1200, ( $< 20$  micro absorbance units for a sample at 0 od), allows for quantification of small spectral differences reproducibly, yielding analytical and control data that has a high degree of accuracy. Accuracies obtained using this technique often approaches that obtained using the primary technique. I am confident that our results can be improved with an improvement in the primary analytical data calibrated against.

FIGURE 1

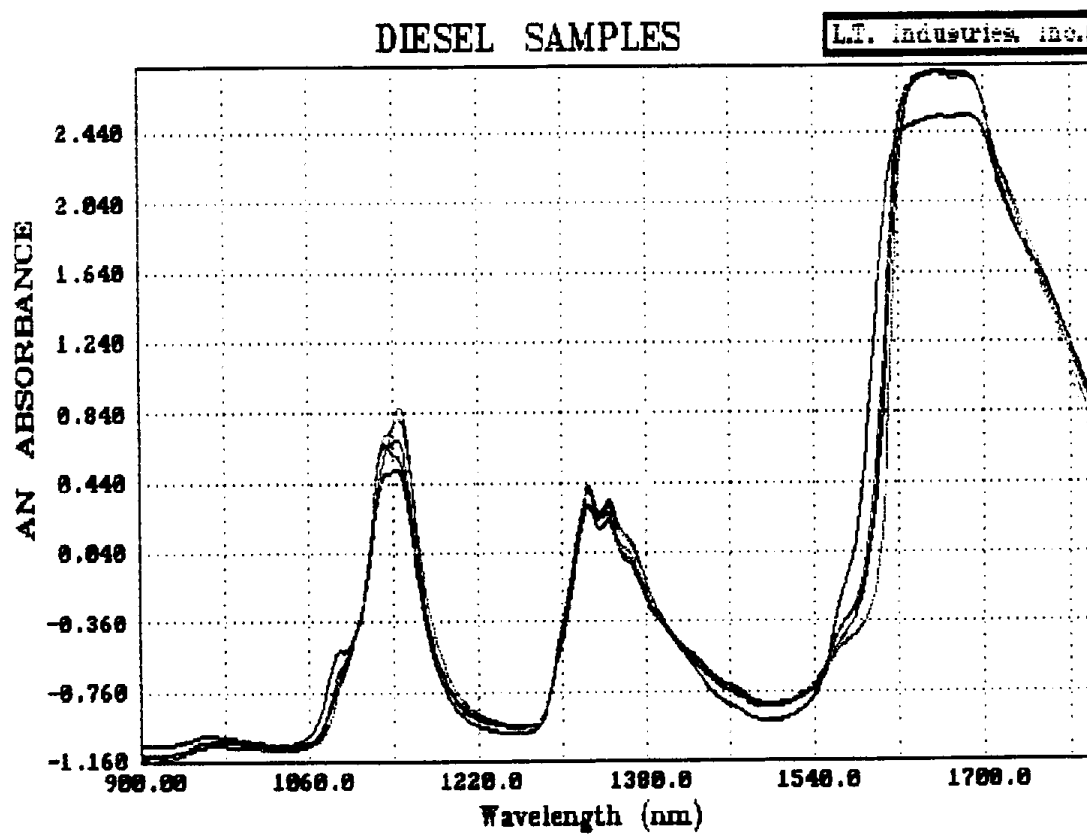


FIGURE 2

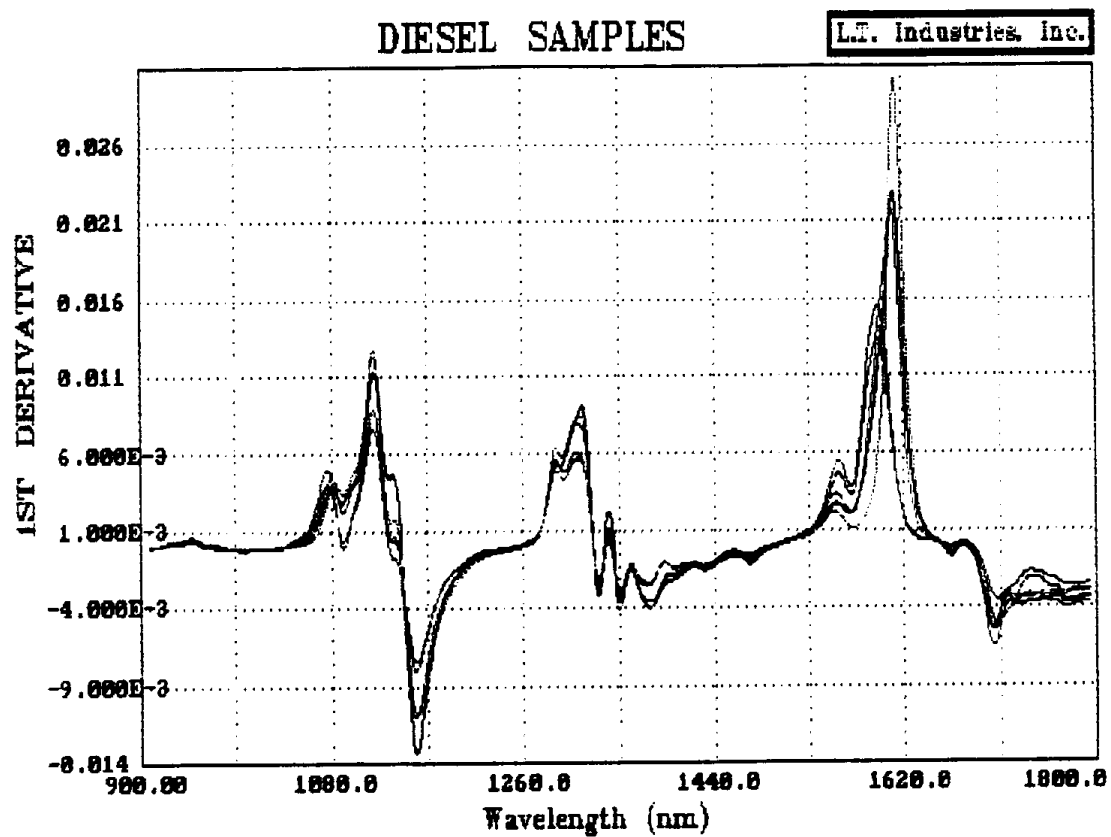


FIGURE 3

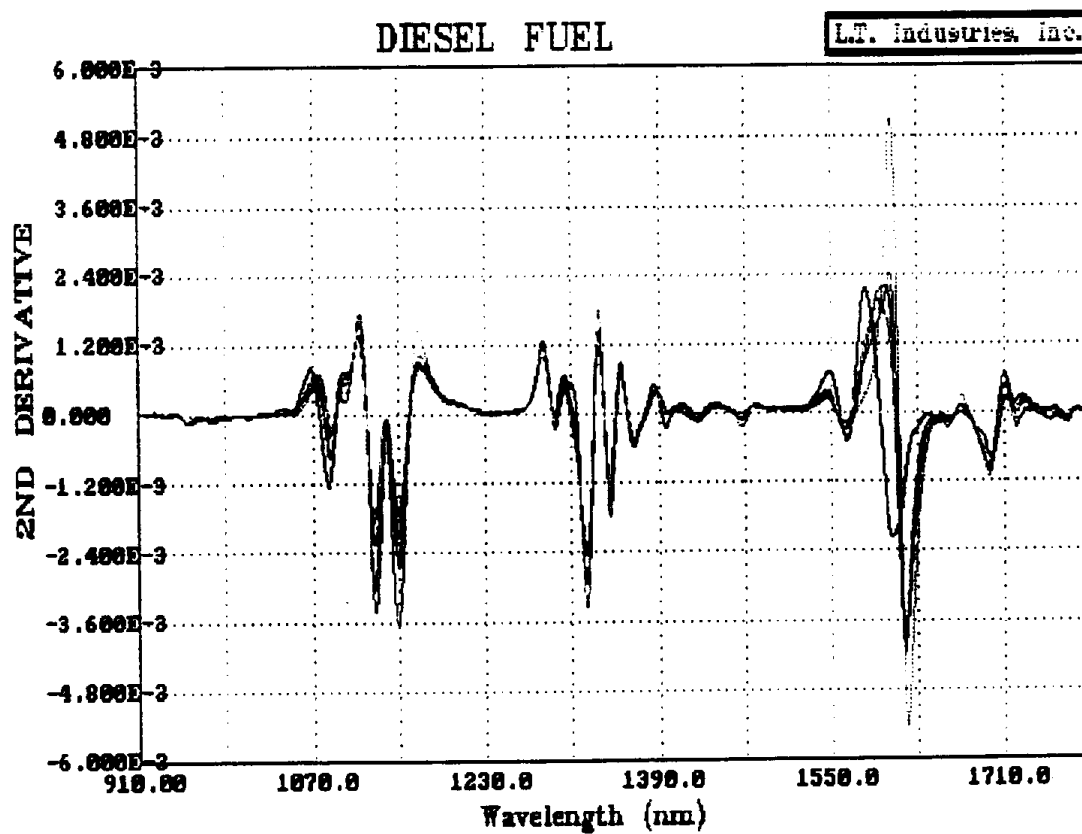


FIGURE 4

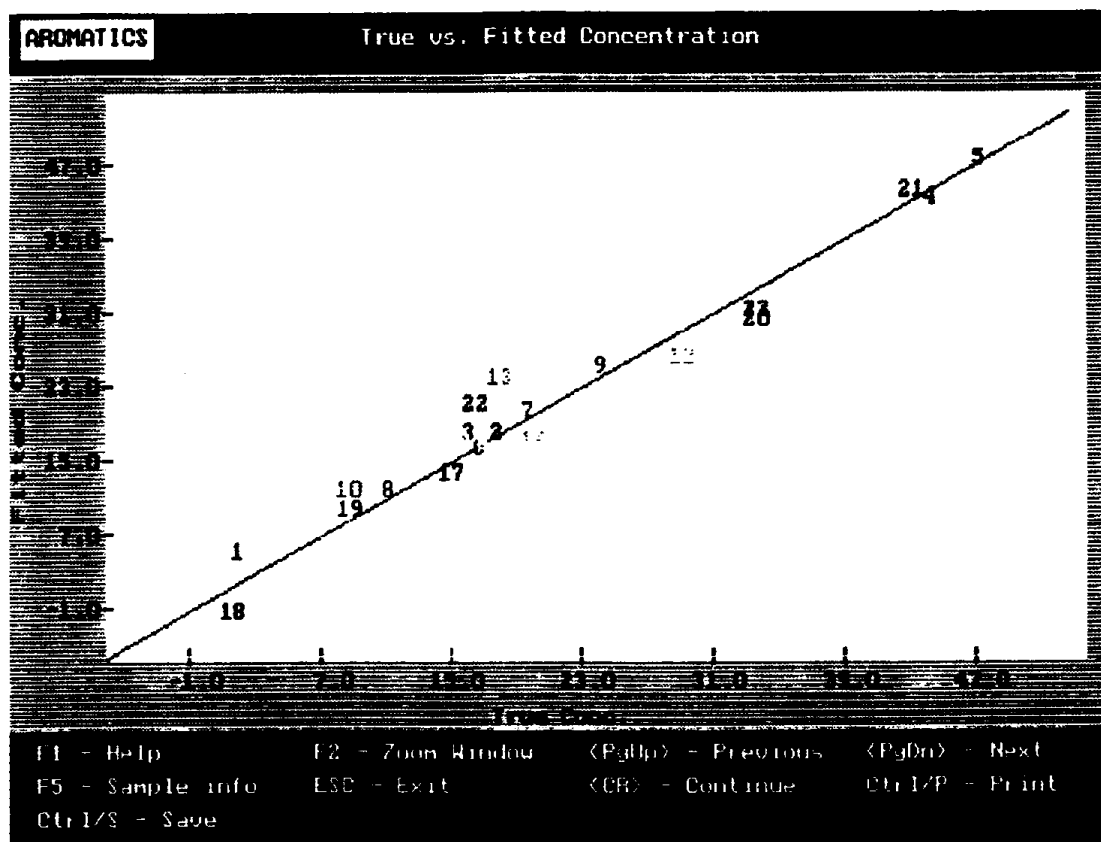




FIGURE 5

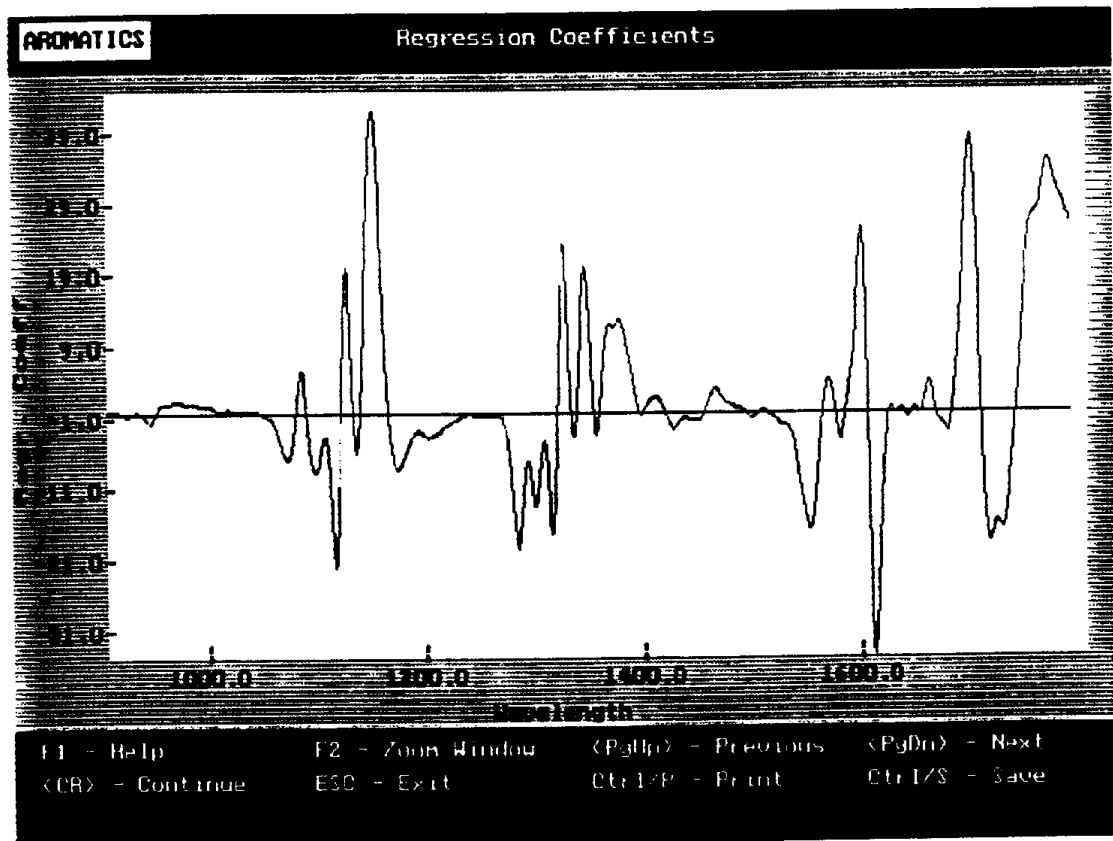


FIGURE 6

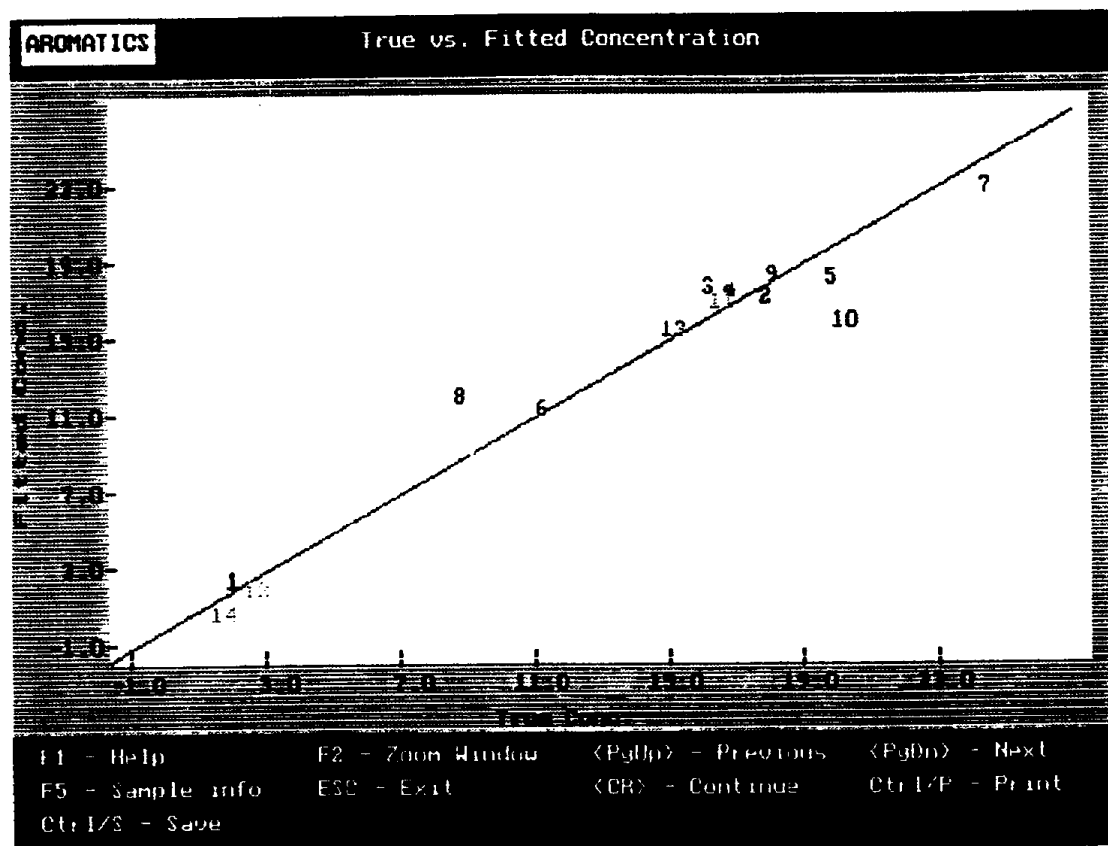
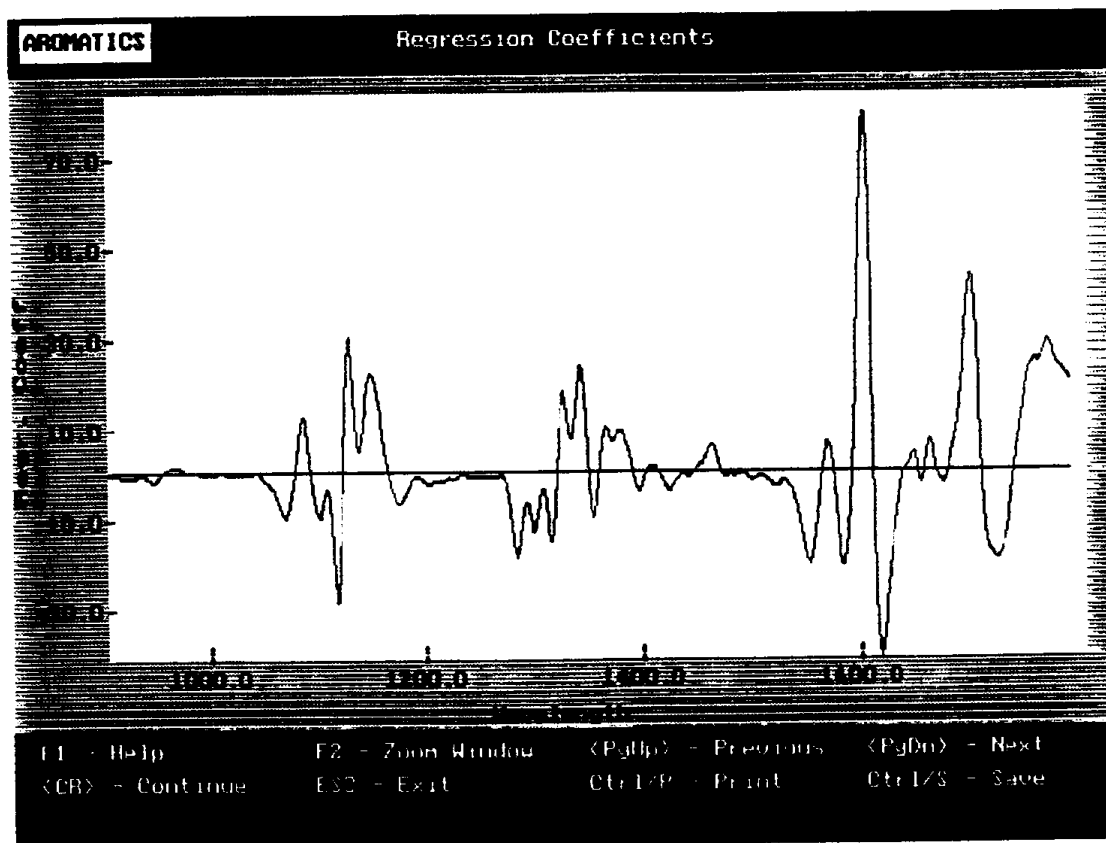


FIGURE 7



**FIGURE 8**

ESC - Exit

FIGURE 9

Sample # 3		SCORES	
1-10			
1-20			
1-30			
1-40			
1-50			
1-60			
1-70			
1-80			
1-90			
1-100			

<CR> - Continue      Ctrl/P - Print



## APPENDIX J. DATA SUMMARY FOR VISUAL COMPARISON





# DATA SUMMARY FOR VISUAL COMPARISON

	Aromatic Area FTIR; ATR	Aromatic Area (Trans)	Aromatic FIA	% Ring Carbon	Aromatic MS	Aromatic SFC	Total UV Aromatic	NMR C-13 Aromatic	Aromatic NMR (H)	New UV Arom
NEG 794		5.246	35.2							
NEG 797	2.7245		37.9							
NEG 796		4.127	33.0							
50% 796	1.6939		15.5							
25% 796	1.2252		7.3							
Kerosene	0.0892		3.2							
Mobil 9014	2.0532		38.3							
Mobil 9015	1.1175		34.4							
Field A	1.5086		32.3							
Field B	0.9422		23.9							
Field C	1.8701		34.8							
Field D	1.3151		35.9							
Field E	1.1726		29.2							
Field F	1.9368		41.3							
Mineral Oil	0.0280	-0.148								
CRC 1	0.7224	1.802	16.6	7.7	16.1			11		7.5
CRC 2	3.1090	7.112	43.9	30.6	45.1			28		20.6
CRC 3	3.0984	6.715	46.9	30.6	43.2			27		14.2
CRC 4	0.9008	2.112	19.0	9.4	16.0			9		6.7
CRC 5		3.118	33.5	13.6	25.7			(16.7)13		6.6
CRC 6	1.3366	3.123	33.5	13.6	25.7			13		11.8
CRC 7		3.124	33.5	13.6	25.7			13		10.8
CRC 8	0.3098	0.731	11.1	3.8	9.0			6		3.3
CRC 9	2.2403	5.415	42.9	22.3	41.1			23		9.8
WX 1	0.7304	2.266	26.02	7.8	25.62	26.35				5.5
WX 2	0.0805	0.000	2.22	1.6	1.79	2.09				0.7
WX 3	0.4787	1.220	20.42	5.4	19.81	20.34				4.1
WX 4	0.1957	0.290	8.40	2.7	6.22	7.65				1.0
WX 5	0.4966	0.858	15.23	5.6	12.22	14.29				3.6
WX 6	0.9149	2.182	22.60	9.6	22.47	24.81				6.3
WX 7	0.6800	1.675	21.03	7.3	19.19	21.39				9.8
CAN A	2.2105	5.096	35.0	22.0		40.3	18.1		28.8	17.0
CAN B	1.3547	3.212	28.9	13.8		30.7	11.4		19.1	8.6
CAN C	1.9013	4.385	41.8	19.1		34.5	12.6		20.9	10.1
CAN D	2.0579	4.703	46.7	20.6		37.1	10.9		24.1	11.4
CAN E	2.2209	5.253	37.0	22.1		42.9	19.6		29.8	17.2
CAN F	2.0295	4.825	33.3	20.3		39.1	12.9		27.2	9.0
CAN G	1.1675	2.906	25.0	12.0		30.4	12.5		21.4	9.1
CAN H	2.6929	6.511	39.1	26.7		46.8	23.6		33.5	22.1
CAN J	1.7941	4.274	44.7	18.0		46.4	17.6		26.2	11.2
CAN M	1.0579	2.560	24.1	10.9		28.4	11.8		18.6	7.8
CAN O	2.8513	6.733	43.7	28.2		49.5	21.2		33.1	19.8
CAN P	2.9896	7.081	44.2	29.5		51.7	22.9		33.7	18.7
CAN Q	5.3371	11.632	64.0	52.1		69.6	35.3		47.2	30.2
CAN R	6.8991	14.332	75.0	67.1		79	41.6		51.9	37.6
CAN S	1.5021	3.687	33.3	15.2		37.6	11.8		14.7	10.6
CAN U	0.8783	2.290					7.9			9.4
CAN V	1.2245	3.032					11.8			10.1
CARB 1	0.2011	0.274	7.1	2.7						1.8
CARB 2	0.0045	0.000	2.0	0.8						0.4
CARB 3	0.2589	0.432	8.7	3.3						2.5
CARB 4	0.7993	1.805	24.1	8.5						5.0
CARB 5	0.2296	0.294	8.8	3.0						2.0
CARB 6	0.9509	1.988	29.0	9.9						8.1
CARB 7	0.0024	0.000	1.8	0.8						0.3
CARB 8	0.7574	1.802	16.4	8.1						6.1
CARB 9	0.5854	1.250	20.0	6.4						4.1
CARB 10	0.7398	1.797	16.0	7.9						6.0
CARB 11	0.0000	0	1.7	0.8						0.3
CARB 12	0.9052	2.284	26.1	9.5						7.8
FL-0416-F	0.3160	0.714	9.4							9.5
FL-0422-F	0.5239	1.155	12.7							4.5
FL-0429-F	1.0425	2.483	24.9					12.1		8.5
FL-0436-F	0.7618	1.978	18.6							10.0
FL-0464-F	0.9070	2.310	20.6							10.5
FL-0467-F	0.7123	1.793	17.6							4.5
FL-0468-F	0.7971	2.114	15.1							10.2
FL-0470-F	0.7460	1.861	19.8							14.3
FL-0502-F	0.0255	0.000	3.7					0		1.0



APPENDIX K. UV SPECTRA WITH AND WITHOUT CETANE IMPROVER



UV AROMATIC SAMPLE WITHOUT CETANE IMPROVER

ReadSamples

tabulate

+ #Scans

Scatter

Method

SaveClear

Print

Quit

Scan directory: VIEW

Start Wl: 190.0 nm

End Wl: 290.0 nm

Overlay scans: [No ]

Autoprint: [No ]

Autosave: [Yes]

Scans per sample: 1

Interval: 5.000 [sec]

Method name: A:\UVCARB

Autosave name: [A:\JCRC2

Sampling device: None

Read average time: 5.00 sec

A:\JCRC2001

Print

↑

↓

←

→

Exit

A:\JCRC2001

Scan

Wl

Abs

Pick

191.0

1.2091

pt

192.0

1.6206

pt

193.0

2.0221

pt

194.0

2.6685

pk

194.0

2.6685

pt

195.0

2.1218

pt

196.0

1.9520

pt

197.0

2.1243

pt

198.0

2.1269

pt

199.0

2.1191

pt

200.0

1.8385

pt

224.0

2.6733

pk

227.0

2.4950

pt

255.0

0.3519

pk

255.0

0.3519

pt

274.0

0.3302

pk

Zoom

ZoomOut

Trace

Function

Autoscale

Annotate

Print

Functions: Scan

3.0000

[Abs]

0.0000

3.0000

190.0

290.0

Wavelength

CRC2 100UL/25ML

NO CETANE IM

BLANK

OFF

[VIS OFF]

RediScan

STATUS

DEVICES

PrtsCrn

TIME

DATE

TEMP

CELL

MATCH

OFF

[UV ON ]

RediRead

DEVICES

PrtsCrn

03:25

06/19/91

N/A

N/A



ReadSamples	Tabulate	+*Scans	Scatter	Method	SaveClear	Print	Quit
HELP							

```

Scan directory: VIEW
Start w1: 190.0 nm
End w1: 290.0 nm
Overlay scans: [No ]

Autoprint: [No ]
Autosave: [Yes]
Autosave name: [A:\JCRC2
Sampling device: None
Read average time: 5.00 sec

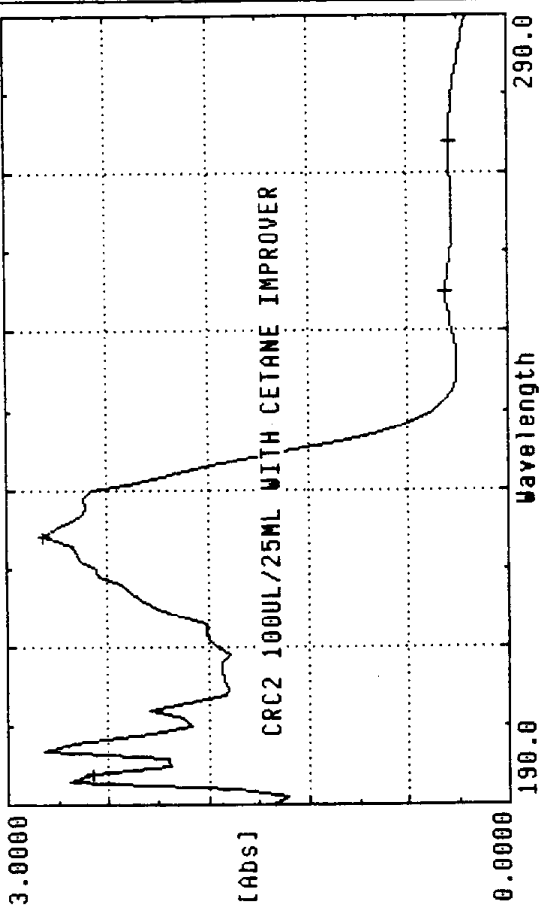
```

A:\CRC2002

Print	↓ ↑ + → Exit	Zoom	ZoomOut	Trace	Function	Autoscale	Annotate	Print
-------	--------------	------	---------	-------	----------	-----------	----------	-------

**Functions: Scan**

w1	Abs	Pick
91.0	1.3227	pt
92.0	1.6337	pt
93.0	2.6382	pt
94.0	2.4924	pk
94.0	2.4924	pt
95.0	2.0266	pt
96.0	2.0383	pt
97.0	2.7813	pt
98.0	2.6125	pt
99.0	2.1335	pt
200.0	1.8980	pt
222.0	2.7803	pk
227.0	2.5502	pt
255.0	0.3725	pk
255.0	0.3725	pt
274.0	0.3457	pk



	TIME	DATE	TEMP	CELL
BLANK	[VIS OFF]	RediScan		
MATCH OFF	[UV ON ]	RediRead		
		PrtScrn	03:36	06/19/91 N/A

